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Energetic Residues on Alaskan Training Ranges

Studies for US Army Garrison Alaska 2005 and 2006

Marianne E. Walsh, Charles M. Collins, Charles A. Ramsey,
Thomas A. Douglas, Ronald N. Bailey, Michael R. Walsh,
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COVER: View across the top of the berm at FP Lampkin at Donnelly Training Area looking downrange toward the Delta River.

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Final report

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Abstract: Soil was collected from Alaskan firing points and impact areas to assess accumulation of 2,4-DNT, NG, RDX, TNT, and/or HMX resulting from live-fire training activities. At each sampling site, the energetic compound was known from previous sampling or from specific training events.

Surface soils at firing points for 105-mm howitzers had part-per-million concentrations of 2,4-DNT resulting from deposition of slivers of propellant from multi-perforated single-base propellant grains. 2,4-DNT was not detectable at a 155-mm howitzer firing point where the propellant formulation was the same, but the propellant grain was single-perforated. Nitroglycerin was detected from tens to hundreds of parts per million at mortar firing points, some of which may have been due to burning of excess propellant. Consistent soil sampling depth to monitor propellant residues is important because 2,4-DNT and NG concentrations decrease sharply with depth. At vegetated firing points, propellant was detectable in mosses and dry, matted grasses, but not in recently emergent leafy vegetation.

To estimate the concentration of high-explosives residues, more mass and increments are needed to overcome the greater spatial and compositional heterogeneity. Particulate HE can persist for many years at upland impact areas, but degradation processes are apparent in a salt marsh impact area.

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Nomenclature

2,4-DNT	2,4-dinitrotoluene
ARDEC	Army Research and Development Command
CRREL	Cold Regions Research and Engineering Laboratory
DAC	Defense Ammunition Center
DRDC	Defence Research and Development Canada
DTA	Donnelly Training Area, Fort Wainwright, Alaska
EL	Environmental Laboratory
EOD	Explosive ordnance disposal
ERF	Eagle River Flats
FRA	Fort Richardson, Alaska
HE	High explosives
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
LO	Low-order detonation
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
rep	replicate
RPD	Relative percent difference
RSD	Relative standard deviation
s	Standard deviation
TNT	2,4,6 trinitrotoluene
UCL	Upper Confidence Limit
USARAK	US Army Alaska
USAGAK	US Army Garrison Alaska
UXO	Unexploded ordnance

Preface

This report was prepared by Marianne E. Walsh, Biogeochemical Sciences Branch (BSB), Cold Regions Research and Engineering Laboratory (CRREL), US Army Engineer Research and Development Center (ERDC), Hanover, New Hampshire; Charles M. Collins, BSB, CRREL; Charles A. Ramsey, EnviroStat, Inc., Fort Collins, Colorado; Thomas A. Douglas, BSB, CRREL; Alan D. Hewitt, BSB, CRREL; Michael R. Walsh, Engineering Resources Branch (ERB), CRREL; Ronald N. Bailey, BSB, CRREL; and Jay L. Clausen, BSB, CRREL.

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At the time this work was performed, Colonel Richard B. Jenkins was Commander and Executive Director of ERDC. Dr. James R. Houston was Director.

1 Introduction

CRREL, in collaboration with EL and DRDC, has sampled the soil on 27 military live-fire ranges in the United States and Canada to determine the identity and distribution of energetic residues. The types of ranges included hand grenade, anti-tank, demolition, bombing, and artillery and mortar impact areas and firing points. A summary of these studies is provided by Jenkins et al. 2005 and 2006. The identity, quantity, and distribution of the residues in the surface soils varied with the type of range. The highest concentrations of HE (high explosives) residues were consistently found at anti-tank ranges where HMX concentrations exceeded 1,000 parts per million around targets and nitroglycerin (NG) concentrations exceeded 1,000 parts per million at firing points. Locations where excess propellant was burned had relatively high concentrations of 2,4-DNT and NG. These two analytes also were found at artillery and mortar firing points at parts-per-million concentrations. Other types of ranges had a more heterogeneous distribution of energetics in that areas of high HE concentration were found sporadically and were associated with events that produced particulate residues. Specifically, demolition areas had residues of RDX from partially detonated C4 blocks. At hand grenade ranges, RDX and TNT (the HE filler) concentrations were generally in the low part-per-million range except where partially detonated grenades were found. Artillery and mortar impact areas are the largest of the training ranges and are remarkably pristine in terms of HE residue, except where ordnance items have malfunctioned.

In 2000, the US Army Garrison Alaska and CRREL initiated studies to investigate and monitor potential contaminants on Army live-fire training ranges. The program began before the distribution of energetics was understood and optimized sampling methods developed. The various studies conducted on Alaskan training ranges have contributed greatly to our understanding of energetics deposition and should result in the sustainable use of training lands.

2 Objective

This report summarizes various studies of energetic residues on USARAK ranges conducted during 2005 and 2006. The sampling objectives were site-specific and are listed in Table 1. We monitored accumulation or persistence of an energetic compound, defined its spatial distribution, and/or refined sampling methods to suit particular site conditions (i.e., vegetated surfaces). In all cases, we revisited locations that either were sampled previously or where an event occurred that we suspected would leave HE or propellant residue.

Table 1. Sampling sites, objectives, and methods.

a. Donnelly Training Area (DTA)		
Location/Date	Objective	Sampling method*
FP Mark/June 2005	Monitor accumulation of 2,4-DNT.	Four samplers, duplicate multi-increment samples from each sampler, 90-m × 120-m decision unit, increment every 15 m.
FP Sally/June 2005	Modify sampling procedure to improve precision of concentration estimates of 2,4-DNT.	One sampler, triplicate 100-increment samples of surface 3 cm and subsurface (3–7 cm), 100-m × 100-m decision unit.
FP Lampkin/June 2005	Monitor persistence of 2,4-DNT and NG. Modify sampling procedure to improve precision of concentration estimates of 2,4-DNT and NG.	Four samplers, one multi-increment each, 70-m × 25-m decision unit, increment every 5 m. Decision unit stratified so that moss-covered area is sampled separately.
FP Bondsteel/June 2005	Determine 2,4-DNT after firing of 155-mm howitzer at “clean” firing point.	One sampler, triplicate multi-increment samples from same 30-m × 30-m decision unit that was sampled on 27 Jan 05. Increment collected every 4 m.
FP Bo-Whale/September 2006	Monitor accumulation of 2,4-DNT.	Two sampling teams; each collected multi-increment samples from 40-m × 40-m decision units around two sets of two howitzer positions and 100 m × 100 m around all four howitzer positions.
OP 7A/September 2006	Monitor accumulation of NG.	Two sampling teams; each collected a multi-increment sample from 45-m × 35-m decision unit.
Washington Range mortar grid/June 2005	Monitor persistence of RDX and TNT.	Two samplers, 50-increment samples from 3-m × 3-m grid that was sampled on 25 July 2000.
Lampkin Range 40-mm berm/June 2005	Monitor persistence of RDX.	Four samplers, one multi-increment sample each, two samples from face of berm and two samples from base of berm. Water sample also collected.
* Multi-increment samples were composed of soil collected at regular intervals across the entire sampling unit.		

Table 1 (cont'd). Sampling sites, objectives, and methods.

b. Fort Richardson (FRA)		
Location/Date	Objective	Sampling method*
FP Fox/September 2005 and 2006	Monitor accumulation of NG. Determine whether sampling method provides reproducible estimates of NG.	Triplicate 100-increment samples from a 22-m × 36-m decision unit, 2-cm depth.
FP Fagan/May 2006	Monitor accumulation of NG.	Quadruplicate 100-increment samples from a 20-m × 30-m decision unit, scoops, 2-cm depth.
FP Cole/May 2006	Monitor accumulation of NG.	Triplicate multi-increment samples from a 15-m × 50-m decision unit, 2-cm depth.
120-mm low-order detonation/ September 2005, May 2006, August 2006	Monitor persistence of RDX and TNT in ERF sediment. Determine whether sampling method provides reproducible estimates of HMX, RDX, and TNT in hot-spot location.	Triplicate 100-increment samples from 30-m × 30-m area around crater.
C4 Craters/July 2004, May 2005, May 2006	Monitor persistence of RDX in ERF sediment.	Multi-increment samples around craters.
* Multi-increment samples were composed of soil collected at regular intervals across the entire sampling unit.		

3 Approach

For each site, the analyte of interest was identified from previous sampling or from an event where the type of ordnance was known. For example, we previously sampled several firing points (FP) at Donnelly Training Area (DTA) that had 2,4-DNT in the surface soils from the firing of 105-mm howitzers (M.E. Walsh et al. 2001, 2003, 2004, 2005). Also, we witnessed winter live-fire activities at DTA and Fort Richardson, Alaska (FRA), and collected snow samples at the firing points to measure propellant residues and at impact points to measure HE residues (M.R. Walsh et al. 2005a, 2005b, 2006). Then, during the spring or summer following the live-fire event, we sampled the surface soils/sediments from the same areas. We applied the procedures that we developed at DTA in 2000 to 2003 to monitor the accumulation of propellant residue at FRA in 2005 and 2006.

Because of the many activities described in this report, the sample collection methods and results for each study are given individually for clarity of presentation. The sample handling and analytical methods are given in Appendix A. Energetic compounds found in specific ordnance items used at the areas we sampled are in Table 2.

Table 2. Ordnance used by the Army at the impact areas and firing points sampled in 2005 and 2006. Based on 13 July 02 to 13 July 03, 1 January 04 to 9 June 05, and 1 January 06 to 1 June 06 ammunition usage reports for DTA and 1 October 2004 to 1 April 2005 for FRA.

Ordnance (DODIC)	Target analyte potentially in residue		Location used and sampled
	Explosive	Propellant	
Small arms			
5.56-mm cartridges (A059, A062, A066, A075)		NG (WC845, WC854, HPC13) PETN in pellet booster	FP Sally, Lampkin, OP 7A
5.56-mm CTG blank (A080)		NG	Lampkin, FP Upper Cole
7.62-mm cartridges (A143, A151)		NG (WC844 WC 846) DNT (IMR 4475)	Lampkin, OP 7A
CTG CAL 0.22 LR ball (A107)		NG	FP Lampkin
CTG, CAL 0.50 4 ball M33/1 TR M17 (A557)		DNT (IMR 5010) NG (WC860)	FP Sally, Lampkin
.50 caliber cartridges (A576)		NG	FP Sally, Lampkin
CTG, CAL .50 ball M2 (A555)		NG (WC860)	Lampkin
CTG CAL .50 blank (A598)		NG (HI SKOR 700X)	Lampkin
40-mm cartridge (B470, B546)	RDX	NG (M2)	Lampkin
40-mm cartridge (TP) (B576, B584)		NG (M2)	FP Sally, Lampkin
Mortars			
CTG 60-mm M888 (B643)	TNT/RDX	(M10)	OP 7A, FP Upper Cole, OP Fagan, ERF impact area
60-mm ILL M721 (B647)		NG (M9)	OP 7A
81-mm ILL (C226)		NG (M9)	FP Upper Cole, ERF impact area
81-mm (TP) (C228)		2,4-DNT (M6)	FP Sally
TP: Target practice round that does not contain high-explosive filler. ILL: Illumination round.			

Table 2 (cont'd).

Ordnance (DODIC)	Target analyte potentially in residue		Location used and sampled
	Explosive	Propellant	
Small arms (cont'd)			
81-mm HE (C256)		NG (M9)	OP 7A
81-mm HE (C868)	TNT/RDX	NG (M9)	OP 7A, FP Upper Cole, OP Fagan, ERF impact area
81-mm ILL (C871)		NG (M9)	OP 7A, OP Fagan
120-mm HE M933 (C623)	TNT/RDX	NG (M45)	OP 7A, FP Upper Cole, FP Lower Fox
Proj & Prop CHG 120 (C801, C805)		NG (M31)	OP 7A
120-mm PRAC FRM931 (CA09)			FP Upper Cole
Howitzers			
105-mm HE (C444, C445)	TNT/RDX	2,4-DNT (M1)	FP Mark, FP Sally, FP Bo-Whale, Washington impact area, ERF impact area
105-mm ILL (C449)		2,4-DNT (M1)	FP Mark, FP Sally, FP Bo-Whale, ERF impact area
105-mm SMK HC (C452, C479)		2,4-DNT (M1)	FP Bo-Whale
105-mm RED SMK (C453)		2,4-DNT (M1)	FP Bo-Whale
105-mm SMK WP (C454)		2,4-DNT (M1)	FP Bo-Whale
105-mm TP C457		2,4-DNT (M1)	FP Bo-Whale
105-mm TP (C511)		NG, NQ (M30)	FP Sally
105-mm SMK HC (C540)			FP Sally
155-mm HEAT (D510)	TNT/RDX	DNT (M1)	FP Sally
TP: Target practice round that does not contain high-explosive filler. ILL: Illumination round.			

Table 2 (cont'd). Ordnance used by the Army at the impact areas and firing points sampled in 2005 and 2006. Based on 13 July 02 to 13 July 03, 1 January 04 to 9 June 05, and 1 January 06 to 1 June 06 ammunition usage reports for DTA and 1 October 2004 to 1 April 2005 for FRA.

Ordnance (DODIC)	Target analyte potentially in residue		Location used and sampled
	Explosive	Propellant	
Howitzers (cont'd)			
155-mm HE M107 (D544)	TNT/RDX	DNT (M1)	FP Mark, FP Sally
Other			
Grenade, hand frag (G881)	TNT/RDX		FP Lampkin
MINE, APERS claymore (K143)	RDX		Lampkin
Rocket motor, 5 in. (J143)		NG (N-4)	Lampkin
C4 (M023)	RDX		Lampkin
Bangalore torpedo (M028)	RDX/TNT		Lampkin
Detonation cord (MD15, M456)	PETN		Lampkin
TP: Target practice round that does not contain high-explosive filler. ILL: Illumination round.			

4 Site-Specific Studies

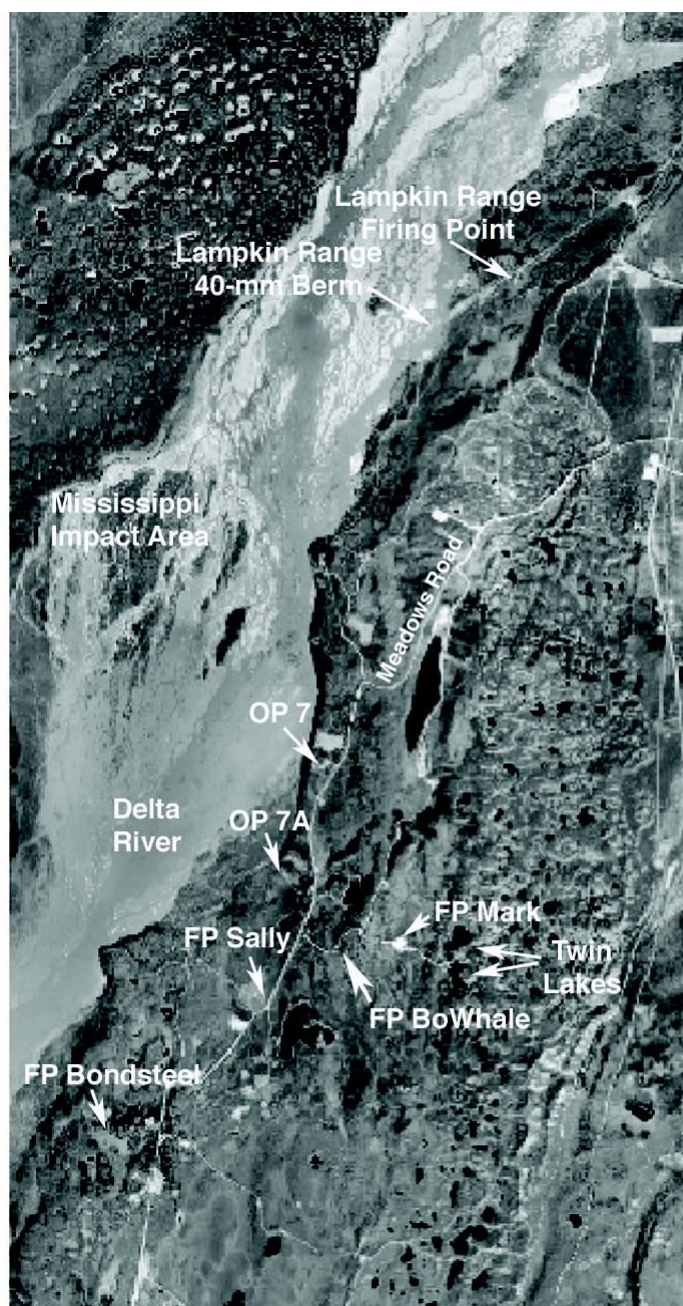
Firing Points

DTA

Summary of Previous Soil Sampling at 105-mm Howitzer Firing Points: DTA has several firing points (Big Lake, Bo-Whale, Sally, Audrey, and Mark) located on the bluffs on the east side of the Delta River from which ordnance is fired into the Washington and Mississippi Impact Areas (Fig. 1). Farther north, FP Lampkin is located on an elevated gravel berm on the floodplain of the Delta River and is used for training with many types of ordnance (Walsh et al. 2004). The Lampkin Range is a multipurpose testing and training range used for firing of small-arms and direct-fire weapons, and for detonations associated with engineer demolitions (Table 2) (US Army AK 2002).

In 2001 and 2002, we sampled firing points Big Lake, Bo-Whale, Sally, Audrey, Mark, and Lampkin (Fig. 1) for 2,4-DNT, a component of M1 propellant used to fire 105-mm and 155-mm projectiles and many other types of ordnance (DAC 2006). 2,4-DNT was easily detectable in most of the surface samples from each of the firing points. Concentrations were typically in the low part-per-million range; however, estimates of 2,4-DNT concentrations from replicate multi-increment and discrete samples from the same location in the field had unacceptably high sampling uncertainty (e.g., some duplicate samples differed by more than a factor of 10). NG was detectable at FP Lampkin and sampling error also was high for this analyte.

In July 2003, we performed several studies to understand and minimize the uncertainty associated with field sampling and laboratory subsampling (M.E. Walsh et al. 2005). Our objective was to obtain a statistically valid estimate of the mean concentration of 2,4-DNT in the surface soil. We met this objective at FP Mark, a sparsely vegetated firing point (Fig. 2) by collecting surface soil samples composed of 50 soil increments from a 90-m × 120-m area. The soil increments were collected at regular intervals across the entire 10,800-m² sampling unit. We obtained an estimate of the mean 2,4-DNT concentration (0.59 µg/g) that had a relative standard deviation of less than 25% (Table 3). The data were adequately described by a normal distribution (Fig. 3), so we could use the Student's t statistic to compute a valid 95% upper confidence limit of the mean, which was 0.7 µg/g.



a. Donnelly Training Area firing points.

Figure 1. Orthophotographs showing sampling locations at Donnelly Training Area (AeroMap US 2003) and Fort Richardson (Aero-Metric 2006).

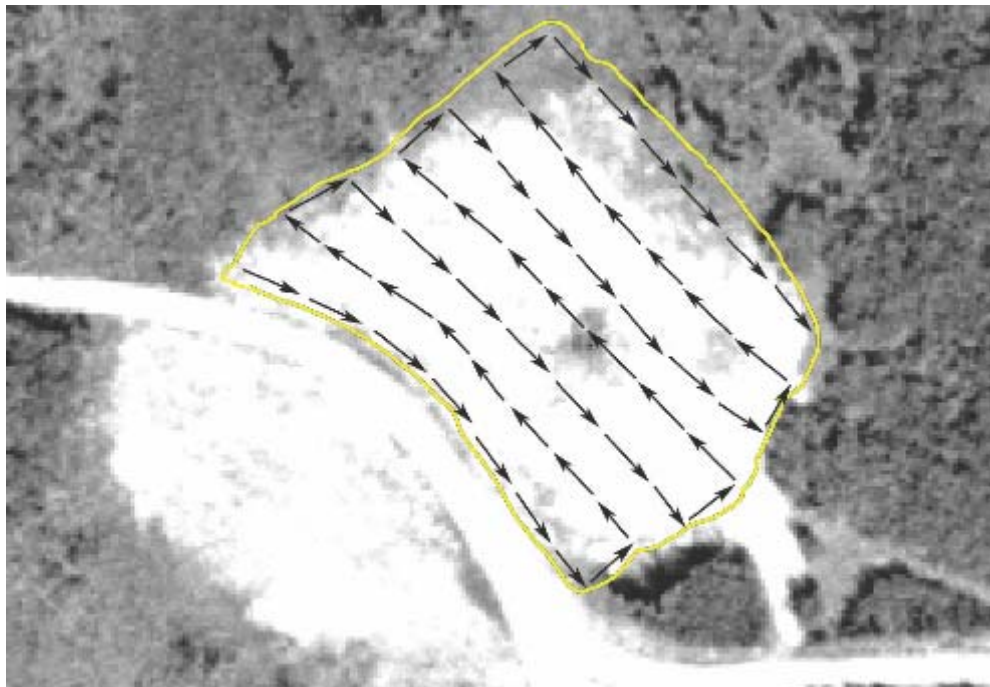


b. Eagle River Flats impact area and neighboring mortar firing points.

Figure 1 (cont'd).



a. Ground view across sampled area of the sparsely vegetated firing point in 2005.



b. Aerial photograph of the 90-m \times 120-m sampled area. Arrows illustrate a path followed by a sampler in which a soil increment would have been collected at each arrowhead.

Figure 2. FP Mark at DTA.

Table 3. 2,4-DNT concentrations determined for multi-increment samples from a 90-m × 120-m area at FP Mark, a sparsely vegetated firing point. The sampling tool was a stainless-steel scoop. Concentrations are based on whole sample extractions.

Sample ID	Total sample mass (kg)	Mass (kg) less than 2 mm	Sampler	Actual number of increments	2,4-DNT (µg/g)
15 July 2003					
FP164	5.31	3.33	CMC	45	0.70
FP165	4.27	2.72	ADH	45	0.62
FP166	4.09	2.69	KB	54	0.43
FP167	4.13	2.74	MEW	47	0.73
FP168	5.62	3.44	MRW	54	0.49
				Mean	0.59
				Variance	0.017
				RSD	22%
				95% UCL	0.73
6 June 2005					
05DTA11	2.51	1.67	CMC	62	1.53
05DTA12	2.13	1.37	CMC	67	1.19
05DTA13	2.33	1.56	CAR	56	1.93
05DTA14	2.38	1.56	CAR	56	2.20
05DTA15	3.14	2.10	MEW	66	1.63
05DTA16	2.64	1.68	MEW	58	0.95
05DTA17	3.16	1.96	JC	78	0.81
05DTA18	2.60	1.63	JC	67	1.23
				Mean	1.43
				Variance	0.23
				RSD	33%
				95% UCL	1.75

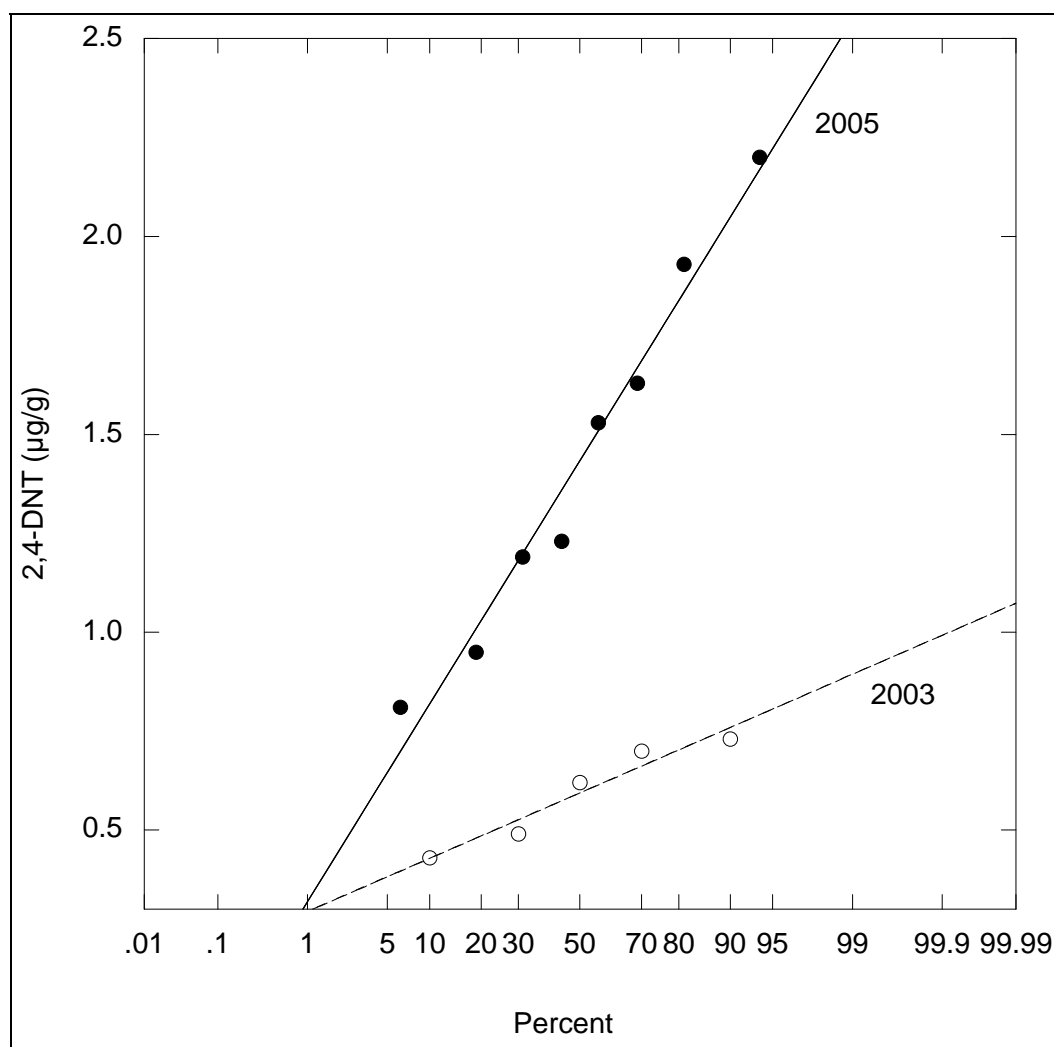


Figure 3. Probability plot of 2,4-DNT concentration estimates from 2005 and 2003 at FP Mark. The linear arrays indicate that the data for each year are adequately described by a normal distribution.

In contrast, at FP Sally (Fig. 4 and 5) and FP Bo-Whale, both heavily vegetated firing points, replicate multi-increment samples did not provide normally distributed estimates of 2,4-DNT concentrations. At FP Sally, the range for seven multi-increment surface samples was 0.14 to 3.7 µg/g and the median was 1.55 µg/g (Table 4). The range of 2,4-DNT concentrations for similarly collected surface samples at FP Bo-Whale was 0.97 to 5.65 µg/g and the median was 2.1 µg/g (M.E. Walsh et al. 2005).



a. Surface view looking northwest across the sampled area in 2005.



b. Aerial photograph showing 100-m × 100-m sampled area.

Figure 4. FP Sally at DTA.



Figure 5. Shrubs, forbs, and grasses sampled for 2,4-DNT at FP Sally in June 2005. The dry, matted grasses had detectable concentrations of 2,4-DNT, but the newly emerged green leaves did not. The last image shows a willow browsed by bison.

FP Lampkin is a gravel berm with some vegetation (Fig. 6), including extensive moss cover on the berm surface farthest from the road. Both NG and 2,4-DNT were detected each time that this firing point was sampled (M.E. Walsh et al. 2001, 2004, 2005). For replicate multi-increment samples collected in 2003, the range of 2,4-DNT concentrations was 0.25 to 1.02 $\mu\text{g/g}$ (Table 6). The mean was 0.55 $\mu\text{g/g}$ with a relative standard deviation of 58%. The range of NG concentrations was 1.7 to 10.3 $\mu\text{g/g}$, and the mean was 4.56 $\mu\text{g/g}$ with a relative standard deviation of 68%.

In June 2005, FP Mark, FP Sally, and FP Lampkin were resampled. At FP Mark, the objective was to monitor the accumulation of 2,4-DNT; at the other two firing points, the objective was to decrease the uncertainty associated with the field sample collection.

Sample Collection and Results in June 2005 at FP Mark: On 6 June 2005, we returned to FP Mark to resample the same area as in July 2003. A new road through the firing point had been graded and appeared to be heavily trafficked (Fig. 2). We used the same AMS #3 (American Falls, Idaho) sampling scoops as in previous years to sample the non-cohesive gravelly surface of FP Mark, where use of a corer is not feasible. The disadvantage of this kind of scoop is that the size of each soil increment is variable, unlike that obtained in more cohesive soil with a sample corer where the diameter of the increment is the inside diameter of the corer and the depth of the sample can be controlled. We used the same sampling method as in July 2003. Each sampler selected a corner of the area to be sampled and collected an increment of surface soil by inserting the AMS sampling scoop approximately 2.5 cm into the soil, twisting the scoop to scribe a circle and loosen the soil, and collecting the soil from scribed area. Then the sampler walked toward the adjacent corner of the area to be sampled and collected an increment of soil every 15 paces. Once at the opposite corner, the sampler turned 90 degrees and walked 15 paces and collected a sample, turned 90 degrees and again traversed the area, collecting increments and counting paces until the entire area was sampled. The actual number of increments varied with the actual path length and stride of each sampler. We had four samplers collect duplicate samples.

Samples masses, number of increments, and 2,4-DNT concentrations for 2003 and 2005 are given in Table 3. In 2005, each sampler collected more increments than in 2003, but the total sample masses were almost half the 2003 samples. Therefore the 2005 soil increments were either shallower or smaller in diameter. We suspect the former because of the compaction of a large portion of the sam-

pled area caused by the new road and subsequent vehicle traffic. The concentration estimates were normally distributed and were all higher than in 2003 (Fig. 3). The higher mean concentration in 2005 (1.43 $\mu\text{g/g}$) versus 2003 (0.59 $\mu\text{g/g}$) could be due to accumulation from additional training and/or shallower sampling depth. The mean for samples collected in July 2002 was 1.39 $\mu\text{g/g}$ when sampling depth was 0–1 cm (Walsh et al. 2004). A consistent sampling depth should be used to monitor 2,4-DNT at firing points because the concentration of 2,4-DNT decreases sharply with depth (Walsh et al. 2004).

Sample Collection and Results in June 2005 at FP Sally: On 9 June 2005, we sampled the same 100-m \times 100-m area as in July 2003 (Fig. 4). In 2003, we had three sampling teams that used 5-cm-diameter corers to obtain 10-cm-long cores every 15 paces across the area to form multi-increment samples. The cores were divided at the root zone so that both a highly organic surface sample and a mineral soil subsurface sample were formed for each collection. The rationale at the time was to estimate the mean of 2,4-DNT in the surface and to determine whether the underlying mineral soil had detectable 2,4-DNT. The length of the root zone varied, and the division between the root zone and subsurface soil was not always distinct. Therefore, the sampling depth varied with each core, thus probably contributing to the sampling uncertainty. We know from previous studies that the highest concentration of energetics is generally within the surface 1 cm. In 2005, to try to decrease the field sampling uncertainty for the estimate of the mean concentration of 2,4-DNT on the surface, we increased the number of increments to 100 and we paid particular attention to the sampling depth by assigning one person to split each core at 3-cm depth and one person to collect all the cores. The corer was 4.75 cm (internal diameter) and was equipped with a stop to set the core length to a maximum of 7.3 cm. Also, to ensure that the entire area was sampled systematically, we used a handheld GPS to track our path back and forth across the hilly terrain.

To determine whether 2,4-DNT was present on the vegetation within the 100-m \times 100-m area, we collected samples of grasses that were growing, grasses that were dry and matted against the ground, and the broad leaves of shrubs and forbs (Fig. 5).



a. View across the top of the berm at FP Lampkin looking southeast across the sampled area. The surface is partially vegetated gravel.



b. Aerial photograph of the Lampkin Range showing sampled area.

Figure 6. FP Lampkin at DTA.

Results from 2003 and 2005 are in Table 4. The total masses for the 2005 samples were between 3.8 and 4 kg and were similar to those of the 2003 samples. The agreement between the field sample replicates was much improved in 2005, either due to the increased number of increments or to better depth control or both. The mean 2,4-DNT concentration for the surface (0–3 cm) was 3.77 µg/g with an RSD of 21%. For the total core the mean was 1.27 µg/g with an RSD of 25%.

The vegetation from growing plants (grasses, shrubs, and forbs) did not have detectable 2,4-DNT (Table 5). However, the dry grass that was matted to the ground had 0.46 µg/g 2,4-DNT. Propellant residue from the winter training activities would accumulate in the snowpack and be deposited on the ground surface during snowmelt, but vegetation growing through the surface interface does not accumulate detectable 2,4-DNT. Bison frequently graze at FP Sally (Fig. 5); the 2,4-DNT deposition from winter training activities would not pose a risk to these grazing animals if they consume the newly emergent leafy vegetation.

Table 5. 2,4-DNT concentrations in vegetation samples from FP Sally in June 2005.

Lab ID	Sample	Total mass (g)	Sampler	2,4-DNT (µg/g)
DTA-V-3	Live grasses	38.8	JC	<0.1
DTA-V-4	Live grasses	17.0	MEW	<0.1
DTA-V-5	Dry, matted grasses	40.3	JC	0.46
DTA-V-6	Green leaves from shrubs and forbs	50.3	MEW	<0.1

Sample Collection and Results in June 2005 at FP Lampkin: On 9 June 2005 we returned to FP Lampkin where we expected to detect 2,4-DNT and NG and to improve the agreement between estimates of mean concentration for these two analytes in replicate field samples. In 2003, we sampled the entire firing point berm surface, which was a 25-m × 90-m area. We used scoops as described above for FP Mark because corers are not appropriate for the unconsolidated, gravelly surface. Increments were collected every seven paces, and the number of increments per sample ranged from 42 to 47 (Table 6). In 2005, we sampled a 25-m × 70-m area and excluded the portion of the berm (Fig. 6) that was farthest from the access road and was covered with moss. We had four samplers, each of whom collected a multi-increment sample with increments taken every five paces across the entire area, and the number of increments ranged from 70 to 97 (Table 6).

Samples of the moss outside the sampling area and green leaves from willow and dandelions from inside the sampling area also were collected (Table 7).

Table 6. Concentrations ($\mu\text{g/g}$) of 2,4-DNT and NG in multi-increment samples from Lampkin Range firing point. The sampling tool was a stainless-steel scoop. Concentrations are based on whole sample extractions.

Lab ID	Mass 2-mm fraction (kg)	Sampler	Actual number of increments	2,4-DNT ($\mu\text{g/g}$)	NG ($\mu\text{g/g}$)
17 July 2003					
FP202	2.62	MEW	42	1.02	1.7
FP203	1.82	ADH	42	0.52	10.3
FP204	2.13	MRW	42	0.37	3.21
FP205	1.76	KB	47	0.25	5.34
FP206	3.36	CAR	44	0.29	2.44
FP207	2.22	CMC	45	0.86	4.34
			<i>Mean</i>	0.55	4.56
			<i>Variance</i>	0.10	9.62
			<i>RSD</i>	58%	68%
			<i>95% UCL</i>	*	*
9 June 2005					
05DTA07	2.10	CMC	97	0.81	14.2
05DTA08	1.44	CAR	70	1.10	9.68
05DTA09	2.07	MEW	89	0.77	9.56
05DTA10	1.58	JC	70	0.93	9.79
			<i>Mean</i>	0.90	10.8
			<i>Variance</i>	0.022	2.26
			<i>RSD</i>	16%	21%
			<i>95% UCL</i>	1.1	13
* Data are not normally distributed.					

Table 7. 2,4-DNT and NG concentrations detected in vegetation at the Lampkin Range firing point.

Lab ID	Sample	Sample extracted	Total sample mass (g)	Sampler	2,4-DNT (µg/g)	NG (µg/g)
DTA-V-7*	Moss	Lab duplicate A*	320	JC	2.2	20.8
		Lab duplicate B			1.8	21.2
DTA-V-1	<i>Salix sp.</i> (willows)	Whole sample	7.14	CMC	<0.1	<0.1
DTA-V-2	<i>Taraxacum sp.</i> (dandelions)	Whole sample	25.4	MEW	<0.1	<0.1
* Sample was air-dried and machine-ground for five one-minute cycles; duplicate 10-g subsamples were taken for solvent extraction.						

The agreement between the field replicates was improved in 2005 for the estimates of 2,4-DNT and NG concentrations (Table 6). The mean 2,4-DNT concentration was 0.90 µg/g with a relative standard deviation of 16% and the mean NG concentration was 10.8 with a relative standard deviation of 21%. Despite the increased number of increments, the sample masses (<2 mm) were generally less than in 2003, implying that smaller increments or shallower sampling depths were obtained. The willow and dandelion leaves did not have detectable 2,4-DNT nor NG, but the moss covering from the far end of the berm (away from the access road) had 2.0 µg/g 2,4-DNT and 21 µg/g NG (Table 7). The moss could potentially act as a collector of the fibrous propellant residue. In any case, sampling precision was improved by the increased number of increments and by stratification so that the moss-covered area was sampled separately. The results from FP Lampkin also demonstrate that attention to sampling depth is important for annual monitoring.

Sample Collection and Results in September 2006 at FP Bo-Whale: In April and May 2006, FP Bo-Whale was used for training with 105-mm HE, ILL, and SMK howitzer projectiles. A total of 1,519 projectiles was fired. Shortly after the firing event, T. Douglas obtained the coordinates of the four gun positions and went to FP Bo-Whale to visually examine the firing point (Fig. 7). The position of each gun was evident from the impression of the howitzer base plates and spades.



a. Impression of the base plate of a 105-mm howitzer at FP Bo-Whale in May 2006. Surface soil samples were collected in September 2006 around four of the howitzer firing positions.



b. Aerial photograph of FP Bo-Whale showing areas sampled in September 2006. The four howitzer positions, numbered 1 to 4, north to south, are symbolized by the yellow \oplus . The orange rectangle outlines the 100-m \times 60-m area encompassing the four firing positions. The yellow squares outline the 40-m \times 40-m areas, each around two firing positions, and the blue square outlines the 40-m \times 40-m area that had no evidence of recent use as a firing position.

Figure 7. FP Bo-Whale at DTA.

In September 2006, the following areas were sampled in duplicate to determine 2,4-DNT in the surface 2 cm of soil (Fig. 7b): a 100-m \times 60-m area surrounding the four gun positions; two 40-m \times 40-m areas, each of which encompassed two firing positions; and a third 40-m \times 40-m area located to the northwest of the four firing positions. The latter area showed no evidence of recent firing activity, but did include an area that we had sampled in 2001 and in which we detected part-per-million concentrations of 2,4-DNT. Samples were taken using a 3-cm-diameter corer. Spacing between increments was 5 m for the 40-m \times 40-m areas and 10 m for the 100-m \times 60-m area.

The concentration of 2,4-DNT was 2.8 $\mu\text{g/g}$ in the duplicate field samples from the 100-m \times 60-m area surrounding the four gun positions (Table 8). This concentration was within the range of concentrations (0.97 to 5.65 $\mu\text{g/g}$) we determined in a nearby 100-m \times 100-m area at FP Bo-Whale in 2003. Similarly, the concentration around guns 3 and 4 was 2.0 $\mu\text{g/g}$. The poor replication of the field replicate samples (4.5 and 23 $\mu\text{g/g}$) around guns 1 and 2 implies the presence of a localized area of much higher concentration that was not represented in each field sample. More increments (closer spacing) would be needed to overcome the spatial heterogeneity for future monitoring. 2,4-DNT was also detectable, but at a much lower concentration, in the area that showed no evidence of recent firing activity. This sampled area overlaps one of the locations that we sampled in 2001 and detected part-per-million concentrations of 2,4-DNT in the surface samples (Walsh et al. 2004).

The samples from Bo-Whale were subsampled, unlike those from FP Mark, FP Sally, and FP Lampkin where the entire field samples were extracted with solvent (Appendix A) as was done in 2003, before adequate sample processing methods were developed for soils with propellant residue. Since 2003, we have found that extended grinding of the soil is needed to pulverize the nitrocellulose propellant fibers (Walsh et al. 2007) and thus reduce the particle sizes and the subsampling variance. The Bo-Whale samples were air-dried and then processed by five 60-s grinding periods in a ring mill.

Table 8. 2,4-DNT concentrations in samples* from FP Bo-Whale (20 September 2006).
The sampling tool was a 3-cm-diameter corer.

Lab ID*	Field sample	Actual number of increments	Sample mass (kg)	Samplers	Lab duplicate	2,4-DNT (µg/g)
O6DTA03	40-m × 40-m guns 1 and 2	64	717	TD/AG	a	21.2
					b	24.9
O6DTA04	40-m × 40-m guns 1 and 2	64	762	SS/AD	a	5.03
					b	3.96
O6DTA05	40-m × 40-m guns 3 and 4	64	684	SS/AD	a	2.10
					b	1.43
O6DTA06	40-m × 40-m guns 3 and 4	64	525	TD/AG	a	2.40
					b	2.79
O6DTA07	100-m × 60-m Gguns 1,2,3,4	60	674	SS/AD	a	2.82
					b	2.57
O6DTA08	100-m × 60-m guns 1,2,3,4	60	522	TD/AG	a	2.93
					b	2.57
O6DTA09	40-m × 40-m NE of guns	64	610	TD/AG	a	0.25
					b	0.32
O6DTA10	40-m × 40-m NE of Gguns	64	798	SS/AD	a	0.06
					b	0.09
* Samples were air-dried and ground for five 60-s cycles; duplicate 10-g subsamples were taken for analysis.						

Sample Collection and Results in September 2006 at OP 7A: OP 7A is a mortar firing point overlooking the Mississippi Impact Area and the Delta River (Fig. 8). No previous soil samples had been collected at this firing point. In April and May 2006, the firing point was used for training with small arms (5.56-mm and 7.62-mm), and 60-mm, 81-mm, and 120-mm mortars. NG is in the propellant (DAC 2006) for the small arms and the 120-mm mortars and is in the ignition cartridge for the 60-mm and 81-mm mortar projectiles.

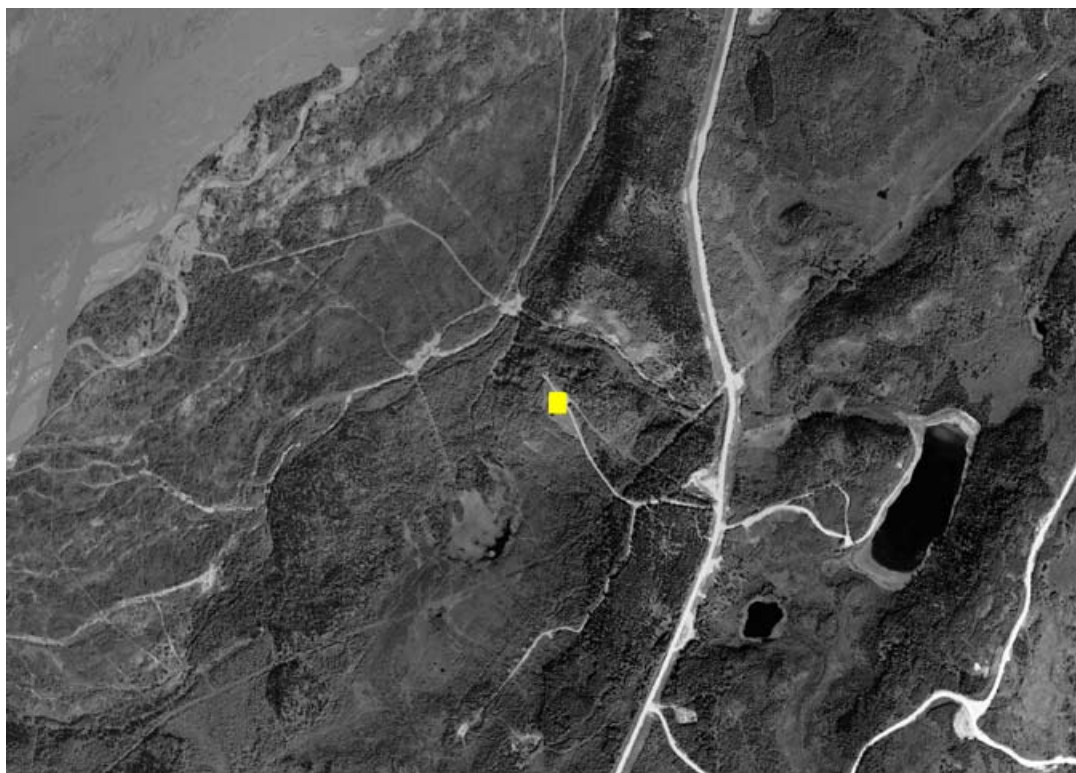


Figure 8. OP 7A at DTA. The yellow rectangle shows the 45-m × 35-m sampled area.

On 20 September 2006, duplicate surface soil samples were collected from a 45-m × 35-m area using the 3-cm-ID corer and a scoop, where needed, to a depth of 2 cm. Each sample consisted of 80 increments. NG was detected at the same concentration (17.5 µg/g) in each field sample (Table 9). These samples were also processed by grinding for five 60-s cycles and the agreement between laboratory replicates was excellent.

Table 9. NG concentrations found in field and laboratory duplicate samples from DTA OP 7A. The 45-m × 35-m area was sampled using the 3-cm-ID corer and a scoop, where the soil was unconsolidated.

Lab ID*	Field rep	Actual number of increments	Total sample mass (kg)	Soil <2-mm plus surface vegetation	Samplers	Lab duplicate	NG (µg/g)	Mean of lab duplicates (µg/g)
06DTA01	1	80	1.48	0.93	AG/TD	a	17.15	17.5
						b	17.9	
06DTA02	2	80	1.33	0.92	SS/AD	a	17.4	17.5
						b	17.6	

* Samples were air-dried and ground for five 60-s cycles; duplicate 10-g subsamples were taken for analysis.

Bondsteel

Summary of previous sampling activities: Bondsteel is a training facility located on the west side of Meadows Road (Fig. 1 and 9) and is not normally used as a firing point for howitzers. However, on 26 and 27 January 2005, sixty 155-mm projectiles were fired over pristine snow during a special mission for the purpose of measuring energetic residues from live-fire exercises (M.R. Walsh et al. 2005a). Each round was fired using 2.54 kg of M1 (single-base, single-perforated) propellant (green bag M3A1). The composition of the M1 propellant (83.34% nitrocellulose, 9.8% DNT, 4.9% dibutylphthalate, 0.98% diphenylamine, and 0.98% potassium sulfate) was the same as that used for the 105-mm howitzer, but the propellant grain geometry is different (US Army 1994). Triplicate 100-increment snow samples were collected from a 30-m \times 30-m area in front of the gun barrel to estimate 2,4-DNT deposition. Based on the mass of 2,4-DNT detected per unit area ($\sim 100 \mu\text{g}/\text{m}^2$) on the snow (M.R. Walsh et al. 2005a), we predicted that if the 2,4-DNT was transferred to the soil as the snow melted, the concentration of 2,4-DNT in soil would be below HPLC detection limits ($<0.03 \mu\text{g}/\text{g}$) (Table 10). This assumption was based on a soil bulk density of $1.5 \text{ g}/\text{cm}^3$ and a sampling depth of 1 cm. Also, trays were positioned on the snow surface to collect residues for microscopic and elemental analysis. Solid material on the trays consisted of round, translucent particles composed of potassium and sulfur (presumably from potassium sulfate in the propellant), metal fragments, fabric from the propellant bags, aggregates of metal and soot, and small ($<0.5 \text{ mm}$) irregular particles of unburned propellant (M.R. Walsh et al. 2005a).

Sample Collection and Results in June 2005 at Bondsteel: On 8 June 2005, we collected triplicate 49-increment samples from the same 30-m \times 30-m area that was in front of the gun barrel. Sampling depth was 1 cm. No definitive peaks were evident for 2,4-DNT in the HPLC-UV chromatograms, so the concentration of 2,4-DNT was less than $0.03 \mu\text{g}/\text{g}$. The extracts also were analyzed by GC-ECD. The detection limit for 2,4-DNT by GC-ECD is $0.001 \mu\text{g}/\text{g}$ in a mineral soil matrix. Detection limits are higher in vegetated matrices due to co-extracted organic compounds that increase the baseline noise of the ECD signal. The estimated detection limit for 2,4-DNT in the Bondsteel samples was $0.01 \mu\text{g}/\text{g}$, but no peaks corresponding to 2,4-DNT were detected (as predicted from the results of the winter sampling).



a. Firing of 155-mm howitzer, January 2005.



b. Sampled area, June 2005.

Figure 9. Bondsteel at DTA.



c. Aerial view of sampled area (30-m × 30-m grid) at FP Bondsteel.

Figure 9 (cont'd). Bondsteel at DTA.

Table 10. Predicted 2,4-DNT concentration in soil at Bondsteel based on the mass detected after live fire of 155-mm howitzers in January 2005 (M.R. Walsh et al. 2005a). The same area was sampled in June 2005 and 2,4-DNT was not detectable (<0.01 µg/g) in the surface soil.

Sample location	Field replicate	Sampler	2,4-DNT mass per area on snow (µg)/(m ²)	Equivalent* soil concentration (µg/g)
30- × 30-m area	1	MRW	121	0.008
	2	MEW	21	0.0014
	3	MRW	96	0.006

* Assumes 1 square meter of soil with a bulk density of 1.5 g/cm³ is sampled to a depth of 1 cm (0.01 m).

$$\frac{121 \frac{\mu\text{g}}{\text{m}^2} \times \frac{1}{0.01\text{m}}}{1.5 \frac{\text{g}}{\text{cm}^3} \times \frac{(100\text{cm})^3}{\text{m}^3}} = 0.008 \frac{\mu\text{g}}{\text{g}}$$

The single-perforated propellant grains used to fire the 155-mm projectiles produced much less residue than the multi-perforated grains used to fire 105-mm projectiles. The multi-perforated grains produce slivers of unburned propellant that can be “expelled from the muzzle” (ARDEC 1999). Also, the barrel of the 155-mm howitzer is longer than the 105-mm, and thus may also contribute to less unconsumed propellant deposition.

FRA

FP Lower Fox

Summary of previous sampling activities: FP Fox (Fig. 1) is located on Fort Richardson and is used primarily for firing 81-mm mortars into the Eagle River Flats impact area (US Army AK 2002). However, in January and February 2005, this firing point was used for training by the 4th/23rd Infantry Regiment with 120-mm mortars (M121) mounted on the new M1129 Light Armored Vehicle III Stryker mortar carriers (Fig. 10). A team from CRREL was present at one of the training events. Samples of snow at the firing and impact points were collected before and after firing to determine the mass of energetic residues deposited on the snow surface (M.R. Walsh et al. 2005b). At FP Lower Fox, triplicate multi-increment snow samples, composed of approximately 100 increments, were collected from a 22-m × 36-m area in front of one of the firing positions following the firing of 40 rounds. NG was detected in each sample and the average mass per unit area of snow surface was 23,000 µg/m² (M.R. Walsh et al. 2005b). If the mass of NG was conserved as the snow melted, concentrations of NG in the soil surface would be around 1 µg/g from this one event and would be detectable by HPLC-UV. Excess propellant was also burned on snow at the firing point. A 14-increment snow sample was collected from the 2-m-diameter burn area with a 10-cm² shovel. The mass of NG detected in this one snow sample was 4.75 g (4.73 g of the NG was in the soot fraction and the remaining 0.02 g was in the aqueous fraction), yielding a surface concentration of 34 g/m² over the burn area. However, if all of the mass of NG was transferred to the soil surface, the equivalent soil concentration would be over 2,000 µg/g within the small burn area.



a. Member of the 4th/23rd Infantry Regiment preparing to fire a projectile from a 120-mm mortar (M121) mounted on an M1129 Light Armored Vehicle III Stryker at FP Fox.



b. Firing of a projectile from the 120-mm mortar.

Figure 10. FP Fox at FRA.



c. Area sampled at FP Fox in September 2005 and September 2006.

Figure 10 (cont'd).

Sample Collection and Results in September 2005 and September 2006 at FP Lower Fox: On 7 September 2005, we sampled surface soil from the same area that was in front of the 120-mm mortar firing position by collecting triplicate multi-increment samples (Fig. 10c). Cores (ID = 4.75 cm) were collected approximately every three paces to a depth of 2 cm over the 22-m × 36-m area. The same sampling team collected the three field samples. The actual number of increments ranged from 100 to 105 and the sample masses ranged from 2.27 to 2.57 kg (Table 11). We repeated the sampling on 2 September 2006 using the same sampling tools but reduced the number of increments by taking increments at approximately 4-m intervals. The actual number of increments was 44 and the sample masses ranged from 1.48 to 1.63 kg.

In September 2005, the mean concentration of NG was 8.7 µg/g and the relative standard deviation was 17%. In September 2006, the mean concentration of NG was 10.0 µg/g and the relative standard deviation was 33%. Even though the uncertainty appears to have increased with fewer increments, these means are essentially equivalent, indicating no positive accumulation of NG between the two sampling events.

Table 11. Concentration of NG at FRA FP Lower Fox that was used to fire 120-mm mortars.
The sampling tool was a 4.75-cm-diameter corer.

Sample ID*	Actual number of increments	Sample mass (kg)	Lab duplicate	NG concentration (µg/g)	Mean of lab duplicates
7 September 2005					
Field Rep 1	100	2.39	a	11.1	10.3
			b	9.58	
Field Rep 2	105	2.27	a	6.59	7.57
			b	8.54	
Field Rep 3	104	2.57	a	8.23	8.16
			b	8.09	
				Mean	8.68
				Variance	2.06
				RSD	17%
				95% UCL	11.1
2 September 2006					
Field Rep 1	44	1.48	a	9.00	9.73
			b	10.5	
Field Rep 2	44	1.54	a	13.0	13.5
			b	14.1	
Field Rep 3	44	1.63	a	7.45	6.88
			b	6.31	
				Mean	10.0
				Variance	11.0
				RSD	33%
				95% UCL	15.6
* Field samples were air-dried and machine-ground for five one-minute cycles; duplicate 10-g sub-samples were taken for solvent extraction.					

FP Fagan

Sample Collection and Results in May 2006: FP Fagan is used as an observation point and mortar firing point for the Eagle River Flats impact area and is located on the bluff above the old explosive ordnance disposal pad (Fig. 1, 11). In May 2006, we sampled a 20-m \times 30-m area of the hard-packed gravelly surface by

collecting increments every 2.5 paces using an AMS sampling scoop to a depth of 2 cm. Two sampling parties each collected duplicate field samples.



Figure 11. View across sampled area (20 m × 30 m) at FP Fagan (FRA) in May 2006.

We detected NG and 2,4-DNT (Table 12). The mean NG concentration was 2.3 $\mu\text{g/g}$ and the relative standard deviation was only 4.4%. NG was the expected analyte because it is a component of the ignition cartridge and of some propellants for mortars. The mean concentration of 2,4-DNT was 0.38 $\mu\text{g/g}$ (39% RSD). The source of the 2,4-DNT at FP Fagan is unknown but may be from small arms containing Improved Military Rifle (IMR) or certain Winchester Cartridge (WC) propellant (DAC 2006).

To estimate the variance associated with dividing a sample under ideal conditions, the less-than-2-mm fraction of one of the field replicates was divided into splits and each split extracted whole without grinding or subsampling. For NG, the ratio between the maximum and minimum concentrations for the ~400-g divisions was 2.2 whereas the ratio for 2,4-DNT was 34. These results imply that a 400-g mass of soil is not sufficient to overcome the compositional heterogeneity for either analyte. We can use these results to obtain an estimate of the constant factor of compositional heterogeneity (Pitard 1993) of this soil matrix, which can then be used to calculate a minimum sample mass. Pitard (1993) states that the

minimum sample mass corresponds to a fundamental error with a standard deviation (FE) of less than 0.16, otherwise skewed data are likely. If we assume that the rotary divider minimized the grouping and segregation error, a constant factor of compositional heterogeneity (IHL) is estimated by

$$IHL = FE^2(M_{sl}) \approx \frac{s_1^2}{x_1^2}(M_{sl}).$$

From data for the ~400-g soil samples in Table 12b, the IHL for NG is estimated to be

$$IHL = \frac{0.30}{2.4^2}(400) = 21.$$

If the estimate of IHL is valid, we can estimate the minimum sample mass corresponding to a fundamental error with a standard deviation of less than 0.16:

$$M_{s_{min}} = \frac{IHL}{FE^2} = \frac{21}{0.16^2} = 820g.$$

Similar calculations for 2,4-DNT yield a minimum sample mass of 11,100 g. We must stress that these are estimates of minimum sample mass, but in general, a 1-kg sample appears to be adequate to represent NG residue, but not for 2,4-DNT residue, at the part-per-million concentrations that appear to be typical at firing points.

FP Upper Cole

Background: FP Upper Cole is located on a bluff on the southwest side of the Eagle River Flats impact area (Fig. 1b). It is used as an observation point and for firing of 60-mm, 81-mm, and 120-mm mortars. In January 2006, Walsh et al. (2006) sampled snow after live fire of high-explosive and illumination cartridges from 81-mm mortars (Fig. 12) and determined an average mass loading of 85,000 $\mu\text{g}/\text{m}^2$ of NG in front of one of the mortars (M.R. Walsh et al. 2006). If we assume that the NG is conserved as the snow melts and is transferred to the top 1 cm of soil (1.5 g/cm^3 bulk density), then the equivalent NG concentration in soil would be 5.7 $\mu\text{g}/\text{g}$.

Table 12. Concentrations of NG and 2,4-DNT in multi-increment samples collected to 2-cm depth from a 20-m × 30-m area at FP Fagan. The sampling tool was a stainless-steel scoop.

a. Field replicates 2, 3, and 4 were ground for five 60-s cycles; duplicate 10-g subsamples were taken for analysis.							
Field rep	Actual number of increments	Sample mass (kg)	Lab duplicate*	NG conc. (µg/g)	2,4-DNT conc. (µg/g)	Mean of lab duplicates	
						NG (µg/g)	2,4-DNT (µg/g)
1	117	4.89		Table 12b	Table 12b	2.4	0.46
2	100	3.43	a	2.0	0.41	2.2	0.42
			b	2.3	0.43		
3	92	3.57	a	2.3	0.20	2.2	0.16
			b	2.1	0.13		
4	88	3.89	a	2.3	0.38	2.2	0.46
			b	2.1	0.54		
*Field samples were air-dried and machine-ground for five one-minute cycles, and duplicate 10-g subsamples were taken for solvent extraction.					Mean	2.3	0.38
					Variance	0.010	0.021
					RSD	4.4%	39%
					95% UCL	2.4	0.55
b. Field replicate 1 was not ground. It was divided on a rotary divider and each division extracted without subsampling to estimate the variance associated with splitting under ideal conditions.							
Division of field rep 1		Mass of division (g)		NG concentration (µg/g)		2,4-DNT concentration (µg/g)	
1		386		2.3		0.14	
2		414		1.5		1.09	
3		413		1.7		0.16	
4		405		3.1		0.17	
5		369		2.8		0.76	
6		426		2.7		0.82	
7		397		3.3		0.04	
8		403		2.4		0.61	
9		411		2.3		0.16	
10		408		2.0		0.52	
11		403		2.9		0.97	
12		411		2.2		0.03	
		Mean		2.4		0.46	
		Minimum		1.5		0.03	
		Maximum		3.3		1.1	
		Variance		0.30		0.15	
		RSD		23%		84%	



a. Close-up of mortar firing.



b. Mortar firing.

Figure 12. Live fire of mortars from Upper Cole (FRA) Point and burning of excess propellant in January 2006.



c. Propellant ready to burn.



d. Burning propellant.

Figure 12 (cont'd).

Almost all the NG detected in the snow samples was from the 61 M301A3 illumination cartridges that were fired. Excess propellant was burned on the snow surface at the firing point (Fig. 12c and d). The firing point was used again in March 2006 for live fire from 60-mm, 81-mm, and 120-mm mortars.

In May 2006, we sampled a 15-m \times 50-m area that included the January 2006 snow sample locations (Fig. 13). We used a 4.75-cm-diameter corer to a depth of 1 to 2 cm to obtain three field replicate samples containing approximately 60 increments each (Fig. 13). The fine-grained surface soil was underlain by rocks, so a sample scoop was needed to retrieve some of the increments.



a. Aerial image showing 15-m \times 50-m area sampled in yellow.

Figure 13. Sampling of surface soil at FP Cole (FRA) in May 2006.



b. Ground view of sampled area in May 2006.



c. Triplicate multi-increment samples. The mean NG concentration was 132 $\mu\text{g/g}$.

Figure 13 (cont'd).

The mean concentration of NG was 130 µg/g at FP Upper Cole (Table 13). The 95% upper confidence level is 190 µg/g. This concentration is higher than the concentration estimated above from the firing of projectiles and is likely due to the burning of propellants at the firing point.

Table 13. Concentrations of NG in multi-increment samples collected to 2-cm depth at FP Upper Cole on 25 May 2006. The area was sampled using the 4.75-cm-ID corer and a scoop, where the soil was unconsolidated.

Field rep*	Actual number of increments	Sample mass (kg)	Lab duplicate	NG concentration (µg/g)	Mean of lab duplicates
1	58	1.03	a	169	165
			b	162	
2	60	1.63	a	93	94
			b	95	
3	57	0.66	a	138	136
			b	134	
				Mean	132
				Variance	1270
				RSD	27%
				95% UCL	192
* Field samples were air-dried and machine-ground for five one-minute cycles; duplicate 10-g sub-samples were taken for solvent extraction.					

Impact Areas

DTA

Background: In June 2005, we revisited two locations where we found high-explosives residues in July 2000 (Walsh et al. 2001). The first location was a gravel berm located in one of the channels of the Delta River that was used as a target in 1998 for 1,800 40-mm grenades (DODIC B470) that contain RDX (Composition A5) as the high-explosive filler (Fig. 14). The second location was the impact point for forty-five 81-mm HE mortar projectiles in February 1992 on the Washington Range. The explosive filler was Comp B.



a. Sampling of berm in July 2000.



b. Remains of the same berm in June 2005.

Figure 14. Impact berm for 1,800 40-mm grenades fired in November 1998 at Lampkin Range (DTA).



c. Water sampling downstream of berm
using a US DH-48 depth-integrating suspended sediment sampler.

Figure 14 (cont'd). Impact berm for 1,800 40-mm grenades fired in November 1998
at Lampkin Range (DTA).

40-mm Berm: In July 2000, we detected RDX along the face of the impact berm. The highest concentration ($1.7 \mu\text{g/g}$) was along the base of the berm in soil collected just below the surface. When we revisited this location in June 2005, the berm was much reduced in size as a result of encroachment and erosion by a channel of the braided river (Fig. 14b). We collected duplicate multi-increment samples from the face of the berm and duplicate multi-increment samples from the toe (horizontal area within 1 m of the face) of the berm. We also collected river water downstream of the berm (Fig. 14c) using a US DH-48 depth-integrating suspended sediment sampler (Rickly Hydrological Company, Columbus, Ohio). The nozzle of the sampler was oriented upstream and the sampler was submerged at a uniform rate to the gravel bottom and raised to the surface at a uniform rate. This process was repeated at multiple locations across the braid of the river downstream from the berm. Thus, the final sample contained water from a cross section of flow.

RDX and HMX were detectable in both samples from the face of the berm; however, the estimated concentrations differed by a factor of 60 for RDX (Table 14). These results, where one sample has a significantly higher concentration than the other, indicate that some particulate HE remains in the eroded remains of this

berm 6.5 years after the grenade test. Given that the concentration of RDX was $1.9 \mu\text{g/g}$ for the 1,119-g sample, the total mass of RDX in the sample was 2.1 mg. If the entire mass of RDX was contained in one spherical particle, the particle diameter would equate to 1.3 mm (given that the density of RDX is 1.82 g/cm^3) and would therefore be similar in size to a grain of sand. The dissolution of particulate explosives by rainfall events has been modeled (Lever et al. 2005) and the model is being verified under field conditions by Taylor (Taylor 2006). Their studies show that loss of mass is primarily controlled by the surface area of the HE particles, so large particulate HE in a well-drained upland site could persist for many years in the relatively dry (annual precipitation less than 30 cm) conditions of Delta Junction. No HE was detectable along the toe of the berm, nor in the river water downstream of the berm.

Table 14. Concentrations of RDX and HMX detected in multi-increment samples collected 9 June 2005 from a gravel berm into which 1,800 40-mm grenades were fired in 1998. The sampling tool was a stainless-steel scoop. The face of the berm was sampled in 2000 and up to $1.7 \mu\text{g/g}$ of RDX was detected.

Lab ID number*	Sample description	Sampler	Increments	Mass (g) <2 mm	Lab duplicate	HMX ($\mu\text{g/g}$)	RDX ($\mu\text{g/g}$)	TNT ($\mu\text{g/g}$)
05DTA01	40-mm berm face	CMC	60	1,119	a	0.28	1.99	<0.02
					b	0.26	1.81	<0.02
05DTA02	40-mm berm face	CAR	62	1,408	a	0.022	0.036	<0.02
					b	0.016	0.032	<0.02
05DTA03	40-mm berm toe (1 m horizontal from base of berm)	MEW	87	1,947	a	<0.02	<0.02	<0.02
					b	<0.02	<0.02	<0.02
05DTA04	40-mm berm toe (1 m horizontal from base of berm)	JC	50	1,060	a	<0.02	<0.02	<0.02
					b	<0.02	<0.02	<0.02

* Samples were sieved and machine-ground for 60 s; two 10-g samples were extracted for analysis.

Washington Range: In July 2000, we sampled four 3-m \times 3-m gridded areas at the coordinates targeted for the test of the M734 multi-option fuse on 81-mm HE mortar projectiles (Fig. 15). We placed one of the grids to encompass the area with the highest density of fins from the mortar projectiles, but we did not detect HE residues above the method detection limit. However, the neighboring grid, which contained no fins, had detectable RDX ($0.37 \mu\text{g/g}$), HMX ($0.051 \mu\text{g/g}$), and TNT ($0.05 \mu\text{g/g}$) (Walsh et al. 2001). We also found the remnants of an 81-mm HE projectile low-order detonation and evidence that other types of ordnance had been fired into this location.

In June 2005, we collected two 50-increment samples from the gridded area that had HE residue in 2000 (Table 15, Fig. 15). One of the samples had nearly twice the mass of the other and had HE residue at concentrations similar to that found in 2000 (Table 15). Again, the poor agreement between field replicates is indicative of particulate HE, most likely from a low-order detonation.



a. Sample grid (3 m \times 3 m) where HE residues were detected in July 2000.

Figure 15. Targeted point for the forty-five 81-mm HE mortar projectiles in 1992 on the Washington Range (DTA).



b. The same area in June 2005.

Figure 15 (cont'd).

Table 15. Concentrations of HMX, RDX, and TNT detected in June 2005 in multi-increment samples from the Washington Range target location for a test using 81-mm HE mortar projectiles in 1992.

Lab ID number*	Sampler	Date collected	Number of increments	Mass (g) <2 mm	Lab duplicate	HMX (µg/g)	RDX (µg/g)	TNT (µg/g)
05DTA05	CMC	8 Jun 05	51	774	a	<0.02	0.13	<0.02
					b	<0.02	0.12	<0.02
05DTA06	MEW	8 Jun 05	50	1,350	a	0.21	0.70	0.12
					b	0.21	0.69	0.11

* Samples were sieved and machine-ground for 60 s; two 10-g samples were extracted for analysis.

FRA

Eagle River Flats 120-mm Low-Order Detonations

Background: In conjunction with the sampling activities for propellant residue at FP Fox on Fort Richardson, discussed previously, we also sampled a portion of the 120-mm mortar projectile impact location within Eagle River Flats. During the firing of the 120-mm mortars, our UXO technician, Mr. Jim Hug, witnessed a

detonation that was atypical. The plume was smaller and the sound of the detonation was muffled, indicating a potential low-order detonation.

Sample Collection and Results for 120-mm Low-Order: In June 2005, we searched the area that was targeted by the Stryker 120-mm mortar crews and found a crater containing the tail assembly of a partially detonated projectile (Fig. 16a) located near the southern edge of a gully. We then searched for pieces of HE scattered outside of the crater. We found 18 chunks of HE that were 2 to 4 cm in their longest dimension, most of which were located between 13.3 m and 18.3 m to the east and south of the crater (Fig. 16b). Most of the larger HE chunks were surrounded by smaller pieces of HE (Fig. 16c). Our UXO technician collected the HE chunks so that we could weigh them. However, the HE chunks proved to be very friable and crumbled into many smaller pieces (Fig. 16d). The pieces collectively weighed 120 g. (The HE was subsequently disposed of with the detonation of UXO items.) We collected a 155-g sediment sample from within the crater, excluding any visible HE particles (Table 16), and detected 2,000 µg/g HMX, 15,000 µg/g RDX, and 8,300 µg/g TNT. The mass of RDX plus HMX accounted for 67% of the sum of the mass of HE, indicating some depletion of TNT from the Comp B as a result of weathering. Unweathered Comp B is 60% RDX (plus HMX as an impurity) and 40% TNT (US Army 1984).

In September 2005, we marked a 30-m × 30-m area on the mudflat around the crater and scatter area of the HE chunks (Fig. 17 and 18). We used a 4.75-mm-ID corer to collect triplicate multi-increment samples to a depth of 3 cm. An increment was collected every three paces so each multi-increment sample would contain approximately 100 cores. The mean concentration of HE in the three field samples was 2.78 µg/g for HMX, 14.1 µg/g for RDX, and 1.32 µg/g for TNT (Table 17). The field sampling error was least for HMX, which is the least soluble of these three compounds, and greatest for TNT, which is the most soluble and most readily biotransformed. Two sediment samples were collected from within the crater, one of the surface (0–3 cm) and one of the subsurface (3–6 cm) (Table 16). The surface concentrations were 950 µg/g for HMX, 7,020 µg/g for RDX, and 2,870 µg/g for TNT. The mass of RDX plus HMX accounted for 74% of the sum of the mass of HE, indicating further weathering of the Comp B. The HE concentrations in the subsurface samples were less than 10% of the surface concentrations. The reduction products of TNT were detected at 8.1 µg/g for 2-Am-DNT and 6.3 µg/g for 4-Am-DNT in the subsurface sample, indicating biotransformation of the dissolved TNT.



a. Crater, tail assembly, scrap, and HE chunks at impact point.



b. View toward the crater (marked with crossed laths) over the area where most of the HE chunks were found. (Each chunk was marked with an orange flag.)

Figure 16. 120-mm low-order detonation.



c. Close-up of one of the HE chunks from the low-order detonation.



d. HE residue from low-order detonation. The 18 HE chunks were friable and were reduced to much smaller particles when collected for weighing.

Figure 16 (cont'd). 120-mm low-order detonation.

Table 16. Concentration of HMX, RDX, and TNT in sediment within a 120-mm low-order detonation crater.

		Concentration ($\mu\text{g/g}$)		
		HMX	RDX	TNT
2 June 2005				
Surface (0–3 cm)*		2,000	15,000	8,300
9 September 2005				
Surface (0–3 cm) ††	Lab rep 1	950	7,030	2,880
	Lab rep 2	950	7,010	2,860
	Mean	950	7,020	2,870
Subsurface (3–6 cm)**	Lab rep 1	86	6,10	208
	Lab rep 2	86	612	210
	Mean	86	611	209
<p>* All of the 155-g sample was extracted with acetonitrile.</p> <p>†† Sample masses were 1,122 g (surface) and 615 g (subsurface). Samples were air-dried and machine-ground for 60 s; duplicate 10-g subsamples were taken.</p> <p>** 8.1 $\mu\text{g/g}$ 2-Am-DNT and 6.3 $\mu\text{g/g}$ 4-Am-DNT.</p>				



Figure 17. Field sample collection within a 30-m × 30-m area encompassing a 120-mm mortar projectile low-order detonation. Multi-increment samples were composed of approximately 100 cores (4.75-cm ID) collected to a depth of 3 cm.

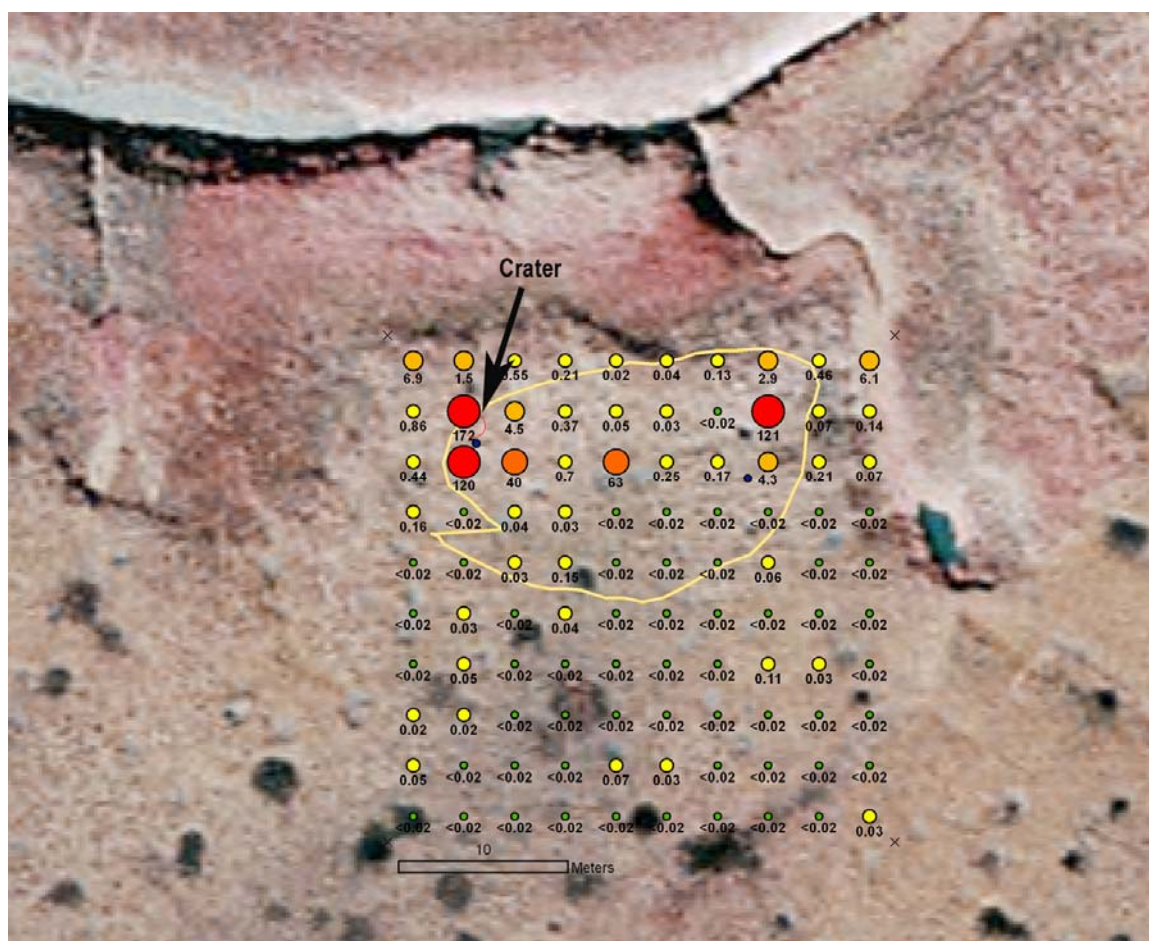


Figure 18. RDX concentrations (µg/g) in 100 discrete samples collected from the same 30-m x 30-m area around a 120-mm low-order detonation. The yellow line demarks the boundary of the area containing the visible chunks of HE.

In May 2006, we returned to the 30-m x 30-m area to resample it with the objective to monitor the persistence of the HE residue in ERF from the February 2005 low-order event. However, more 120-mm mortars had been fired during the previous March and five more 120-mm mortar projectile low-order detonations were found nearby on the east side of the river, one of which was only 13 m west of the 30-m x 30-m sample area. Six more low-order detonations were subsequently found on the west side of the river. Within the 30-m x 30-m area around the first low-order crater, we collected triplicate multi-increment samples using the same procedure as the previous fall. Two of the field replicates had HMX and RDX concentrations similar to the fall results, but significantly more TNT (Table 17). The third field replicate had considerably higher concentrations of all three compounds. We suspect that this apparent increase in concentrations was due to additional input of HE from the closest March 2006 low-order detonation.

Table 17. Concentrations of HMX, RDX, and TNT in multi-increment samples collected from a 30-m × 30-m area around a 120-mm mortar projectile low-order detonation. The sampling tool was a 4.75-mm-ID corer.

Field rep	Sampler	Actual number of increments	Sample mass (kg)	Lab duplicates*	HMX conc. (µg/g)	RDX conc. (µg/g)	TNT conc. (µg/g)
September 2005							
1	CMC/RNB	97	5.81	a	2.23	10.4	1.04
				b	2.28	10.3	1.02
2	KB/JH	100	6.16	a	3.33	17.1	0.71
				b	3.31	18.0	0.72
3	KB/JH	100	6.33	a	2.79	15.1	2.42
				b	2.76	14.0	2.01
			Mean of field reps		2.78	14.1	1.32
May 2006							
1	MRW/MEW	75	4.07	a	3.09	13.6	4.31
				b	2.94	13.6	4.30
2	AG/SP	96	3.97	a	3.42	18.1	5.52
				b	3.95	17.1	5.37
3	CMC/	120	8.30	a	7.47	46.9	17.2
				b	7.10	42.7	18.2
			Mean of field reps		4.66	25.3	9.15
August 2006							
1	GA/MEW	127	7.31	a	0.83	2.94	0.06
				b	0.78	2.88	0.05
2	MRW/TAD	100	5.54	a	1.63	5.59	0.25
				b	1.64	7.03	0.30
3	CMC/SS	100	4.18	a	2.75	11.8	1.17
				b	2.74	11.5	1.09
4	GA/MEW	65	3.90	a	2.65	8.53	0.32
				b	2.48	8.52	0.34
			Mean of field reps		1.94	7.35	0.45
* Samples were air-dried and machine-ground for 60 s; duplicate 10-g subsamples were taken.							

In August 2006, the 30-m × 30-m area was sampled again. Since the end of May, the area had been inundated at least five times during a series of flooding tides that occurred from 10 to 14 August 2006, and the cumulative rainfall was 18 cm. Four replicate multi-increment samples were collected using the same procedure as the previous two sampling events. Also, 100 discrete samples were collected to define the spatial distribution of the residue.

The estimated HMX concentrations for the four field replicates ranged from 0.81 to 2.75 µg/g and the RDX ranged from 2.9 to 11.7 µg/g, thus the agreement between the field replicates was marginal for HMX and RDX. For TNT, the estimates ranged from 0.06 to 1.1 µg/g, thus the agreement was poor for TNT (Table 17). The large uncertainty associated with the TNT concentration estimates indicates an increase in heterogeneity between the May and August sampling events, most likely as a result of TNT dissolution and transformation. For all three analytes, the maximum concentration detected in August was less than the minimum detected in May.

For the 100 discrete samples, HMX and RDX were detectable in 46 samples and TNT was detectable in only seven samples (Table A1), giving a median concentration of less than the detection limit (0.02 µg/g) for all three analytes (Table 18). These results emphasize the futility of the use of discrete samples to represent HE concentrations. The extreme spatial heterogeneity of the HE residue is evident from the map of RDX concentrations (Fig. 18).

The dynamics of the salt marsh environment that include periodic inundation and fluctuating redox potentials most likely result in conditions that dissolve and reduce TNT, RDX, and, ultimately, HMX. Despite the uncertainty associated with the concentration estimates derived from the multi-increment samples, the data suggest that all three analytes are not persistent in the salt marsh environment. All three of these energetic compounds biotransform in anaerobic environments (McCormick et al. 1976, 1981, 1984; Esteve-Nunez et al. 2001; Ringelberg et al. 2003). TNT is the most readily dissolved and biotransformed, and most likely persists only in particulate form on the mudflat, resulting in the poor agreement between the August 2006 multi-increment samples and low number of detections in the 100 discrete samples. Monitoring the attenuation of these compounds would entail repeated annual sampling of this area.

Table 18. Summary statistics for 100 discrete samples taken at 3-m intervals from a 30-m × 30-m area encompassing the 120-mm low-order detonation crater and chunk scatter area on the mudflat. Concentration estimates for the individual samples are given in Appendix Table 1.

Date of sample collection was 23 August 2006.

Summary statistics		HMX	RDX	TNT
Minimum concentration (µg/g)		<0.02	<0.02	<0.02
Maximum concentration (µg/g)		39.9	172	1.62
Median concentration (µg/g)		<0.02	<0.02	<0.02
Number of samples above detection limit		46	46	7
	Sum of masses			
	Sediment (g)	HMX (µg)	RDX (µg)	TNT (µg)
	2,342	3,810	12,900	46.6
	Grand mean concentration (µg / g)			
		HMX	RDX	TNT
		1.63	5.52	0.02
Core diameter was 3 cm to a depth of 3 cm. Average mass for cores was 23.4 g; median mass was 24.2 g.				

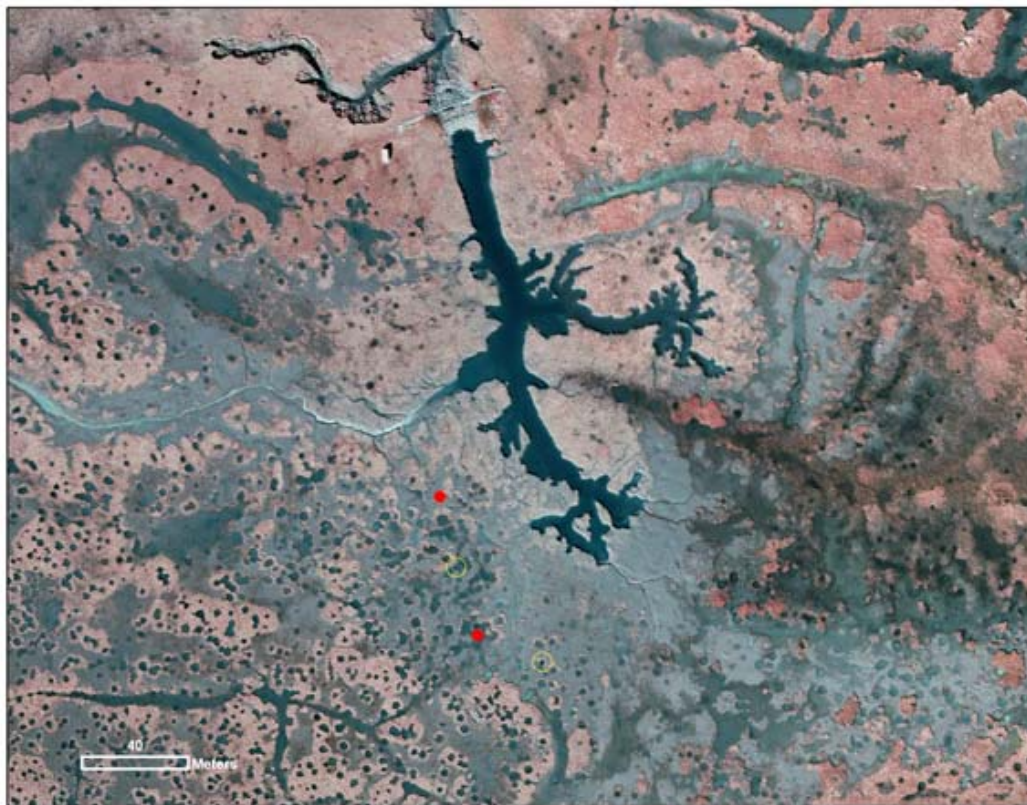
C4 Low-Order Detonations

Background: In July 2004, four individual blocks of C4 (RDX) were detonated on the surface of the mud in Eagle River Flats. The area where the detonations occurred was previously a shallow pond that was highly contaminated with white phosphorus. The pond was drained in 1996 by opening a channel to an advancing gully. After the pond drained, the surface sediments dried intermittently, and white phosphorus became undetectable in the surface sediments. The subsurface sediments still contain some white phosphorus that could be exposed if the surface sediments are disturbed. The purpose of the detonations was to determine whether white phosphorus would be detectable within the crater or the sediment ejected from the crater. The C4 detonations were designed to simulate disturbance of the sediments that would be caused by a point-detonating projectile. Two of the blasts were unintentional low-order detonations that dispersed pieces of C4 over the mud surface. All visible chunks of C4 from the low-order detonations were collected by the UXO technician for disposal.

Sample Collection and Results: The detonation craters were numbered 1 through 4; craters 1 and 3 were the low-order detonations. Sediment that was collected from each crater on 21 July 2004, the day of the detonations, was analyzed for both white phosphorus and high explosives (Fig. 19).

No white phosphorus was detected in or around the four craters. No explosives residues were detectable in the craters corresponding to the high-order detonations. The sediment sample from crater 1, a low-order detonation, had 1,910 $\mu\text{g/g}$ RDX and 230 $\mu\text{g/g}$ HMX, and the sample from crater 3 had concentrations about ten times lower (Table 19).

The sediment within a 1-m radius surrounding craters 1 and 3 was sampled (Fig. 19b) in May 2005 and again in 2006 to monitor the persistence of HMX and RDX. Concentrations declined in both craters for both analytes (Table 19). HMX and RDX appear to be declining at similar rates within each crater. However, the rate of decline appears to be greater in crater 1 than in crater 3, perhaps as a result of different sediment moisture conditions and thus anaerobic/aerobic status of the sediments.



a. Aerial image showing locations (red circles) of craters 1 (north) and 3 (south).

Figure 19. Craters from low-order detonations of blocks of C4 at Eagle River Flats.



b. Cavities formed by sampling within 1 m of crater 3.

Figure 19 (cont'd).

Table 19. Concentrations of HMX and RDX in sediment from Eagle River Flats following the low-order detonations of blocks of C4.

Sample location and date	Lab duplicate*	HMX	RDX
Crater 1			
21 July 2004	a	232	1,916
	b	228	1,904
26 May 2005	a	8.3	56.2
	b	8.0	55.5
25 May 2006	a	1.4	4.3
	b	1.5	3.9
Crater 3			
21 July 2004	a	22.7	174
	b	23.5	180
26 May 2005	a	15.4	95
	b	16.8	100
25 May 2006	a	3.9	20
	b	3.9	22
* Samples were air-dried and machine-ground for 60 s; duplicate 10-g subsamples were taken.			

5 Discussion

Firing Points

Deposition of propellant residue at firing points is an unavoidable consequence of live-fire training. In soil samples that we have collected from Alaskan training ranges from 2000 to the present, 2,4-DNT has consistently been detected at low parts-per-million concentrations at 105-mm firing points and NG at tens to hundreds of parts per million at mortar/multipurpose firing points. The residue produced by the open burning of excess propellant creates localized areas of concentrated NG and 2,4-DNT; disposal practices could be modified to minimize the mass of residue transferred to the soil and potentially to water.

Iterative sampling of 105-mm firing points at DTA does not show a significant accumulation of 2,4-DNT over the years, indicating that degradation processes are active. These processes would entail dissolution and leaching of the 2,4-DNT from the nitrocellulose matrix followed potentially by biodegradation (Fortner et al. 2003). Likewise, NG propellant residue would be expected to leach and possibly biodegrade (Marshall and White 2001, Yost 2004). We have multiple-year data from FP Lampkin where estimated NG concentrations were highest in 2002 (50 µg/g) and lower in 2003 (4.6 µg/g) and 2005 (11 µg/g). At FP Fox, NG concentrations were similar for the two years when samples were collected (2005 [8.7 µg/g] and 2006 [10 µg/g]). The highest NG concentrations were at FP Cole (130 µg/g) where we know that both live-fire and propellant burning took place.

Monitoring of the accumulation of propellant residues would be a worthwhile component of a training range management plan, especially at firing points that are used as bivouac areas and those located near water. Also, long-term monitoring would yield insight into the cumulative environmental loading over time as training activities change. Fixed firing points that are used intensively could receive propellant deposition at a higher rate than the environmental conditions degrade it, resulting in accumulation, as measured by soil concentration and potential migration of propellant residue to groundwater. The concentrations of 2,4-DNT and NG at some of the firing points that we sampled exceed the preliminary remediation goals listed by EPA Region 9, which are 0.72 µg/g for 2,4-DNT and 35 µg/g for NG (USEPA 2004a, b). These goals do not address the impact to groundwater or to ecological receptors; rather, they are based on direct contact pathways (ingestion, dermal contact, and inhalation). They may be unre-

alistic for the site conditions and exposure scenarios at a training range, but when soil concentrations far exceed these goals, further evaluation is warranted to protect both human health and the environment.

We have found that for data to be comparable from year to year, sampling depth must be consistent because the concentration of 2,4-DNT and NG generally decreases sharply with increasing depth (Table 4). Vegetated firing points present a much more complicated sample matrix, but we found at FP Sally that 100-increment samples from a 100-m \times 100-m area produced concentration estimates with a relative standard deviation of 25%. Moss and dry, matted vegetation had detectable 2,4-DNT, but the recent emergent leafy vegetation did not. If a firing point differs markedly in vegetation cover, the decision unit could be stratified as at FP Lampkin where one set of samples was from the sparsely vegetated gravel surface and a moss-covered area was sampled separately.

In terms of laboratory processing procedures, machine grinding for five 60-s cycles reduces laboratory subsampling uncertainty for propellant residue (2,4-DNT and NG) (Walsh et al. 2007), but not to the extent achievable for the crystalline explosives (HMX, RDX, and TNT) (Tables 20 and 21). The laboratory uncertainty for propellant residue is similar in magnitude to the field sampling uncertainty for firing points.

The soil sample mass needed to represent the proportion of propellant particulate residue to the soil matrix is estimated to be at least 1 kg. To maintain the field sample integrity, the entire field sample needs to be processed in the laboratory.

Impact Areas

High-explosive ordnance detonations of mortar and artillery projectiles normally leave very little energetic residue in the impact area (Jenkins et al. 2002; Hewitt et al. 2005; M.R. Walsh et al. 2005a, 2005b, 2006). Occasionally, a malfunction will produce either unexploded or partially (low-order) detonated ordnance. Partially detonated ordnance consists of pieces of the projectile body and chunks of the explosive filler that may be scattered up to tens of meters from the impact point (Taylor et al. 2004a, Jenkins et al. 2005). Both unexploded and partially detonated ordnance represent potential sources of residue that could migrate with surface or groundwater (Taylor et al. 2004b). However, it is the partially detonated ordnance that represents a more immediate threat because the energetics are exposed to the weather and the total exposed surface area is larger for the partially detonated than for the unexploded ordnance (Lever et al. 2005).

a. 2,4-DNT						
Location	Number of field samples (n)	Mean of field samples (µg/g)	RSD field samples (n ≥ 3)	RPD field samples (n = 2)	Mean of lab duplicates	RPD for lab duplicates
FP Mark (90 m × 120 m)	8	1.4	34%			
FP Sally (100 m × 100m, 0- to 3-cm depth)	3	3.8	21%			
FP Sally (100 m × 100 m, 0- to 7.3-cm depth)	3	1.3	25%			
FP Lampkin (soil)	4	0.90	17%			
FP Lampkin (moss)	1				2.0	20%
FP Bo-Whale (100 m × 100 m)	2	2.7		2.0%	2.7 2.8	9.3% 13%
FP Bo-Whale (40-m × 40-m, Guns 1 and 2)	2	14		135%	23 4.5	16% 24%
FP Bo-Whale (40-m × 40-m, Guns 3 and 4)	2	2.2		38%	1.8 2.6	38% 15%
FP Bo-Whale (40-m × 40-m, NE of guns)	2	0.18		117%	0.29 0.08	25% 40%
FP Fagan	4	0.38	39%		0.46 0.42 0.13 0.54	WSE* 4.8% 42% 35%

* Whole sample extraction of 12 splits.

Table 20 (cont'd).

b. NG						
Location	Number of field samples (n)	Mean of field samples (µg/g)	RSD (n ≥ 3)	RPD (n = 2)	Mean for lab duplicates	RPD for lab duplicates
FP Lampkin (soil)	4	11	21%			
FP Lampkin (moss)	1				21	1.9%
OP 7A	2	17.5		0%	17.5 17.5	4.3% 1.1%
FP Fox (100 increments)	3	8.7	17%		10.3 7.6 8.2	15% 26% 1.7%
FP Fox (40 increments)	3	10	33%		9.7 13.5 6.9	15% 8.1% 17%
FP Fagan	4	2.3	4.4%		2.4 2.2 2.2 2.2	WSE* 14% 9.1% 9.1%
FP Cole	3	132	27%		165 94 136	4.2% 2.1% 2.9%

* Whole sample extraction of 12 splits.

Table 21. Summary table comparing uncertainty associated with field samples and laboratory subsamples.

a. RDX						
Location	Number of field samples (n)	Mean of field samples ($\mu\text{g/g}$)	RSD (n \geq 3)	RPD (n = 2)	Mean for lab duplicates	RPD for lab duplicates
Lampkin Range 40-mm target berm	2	0.97		193%	1.9 0.034	9.5% 12%
Washington Range mortar impact point	2	0.41		139%	0.13 0.70	8.0% 1.4%
ERF 120-mm mortar low-order crater (0- to 3-cm depth)	1				7020	0.3%
ERF 120-mm mortar low-order crater (3- to 6-cm depth)	1				611	0.3%
ERF 120-mm mortar low-order (30 m \times 30 m) September 2005	3	14	28%		10 18 15	1.0% 5.0% 7.3%
ERF 120-mm mortar low-order (30 m \times 30 m) May 2006	3	25	67%		14 18 45	0% 5.7% 9.4%
ERF 120-mm mortar low-order (30 m \times 30 m) August 2006	4	7.4	50%		2.9 6.3 12 8.5	2.1% 23% 2.6% 0.1%
C4 Crater 1 2004	1				1,910	0.6%
C4 Crater 1 2005	1				56	1.3%
C4 Crater 1 2006	1				4.1	9.8%
C4 Crater 3 2004	1				177	3.4
C4 Crater 3 2005	1				98	5.1
C4 Crater 3 2006	1				21	9.5

Table 21 (cont'd).

b. HMX						
Location	Number of field samples (n)	Mean of field samples (µg/g)	RSD (n ≥ 3)	RPD (n = 2)	Mean for lab duplicates	RPD for lab duplicates
Lampkin Range 40-mm target berm	2	0.14		174%	0.27 0.019	7.4% 32%
Washington Range mortar impact point	2	0.12*		165%	0.21 <0.02	0% 0%
ERF 120-mm mortar low-order crater (0- to 3-cm depth)	1				950	0%
ERF 120-mm mortar low-order crater (3- to 6-cm depth)	1				86	0%
ERF 120-mm mortar low-order (30 m × 30 m) September 2005	3	2.8	19%		2.3 3.3 2.8	2.2% 0.6% 1.1%
ERF 120-mm mortar low-order (30 m × 30 m) May 2006	3	4.7	49%		3.0 3.7 7.3	5.0% 14% 5.1%
ERF 120-mm mortar low-order (30 m × 30 m) August 2006	4	1.9	46%		0.81 1.6 2.7 2.6	6.2% 0.6% 0.4% 6.6%
C4 Crater 1 2004	1				230	1.7%
C4 Crater 1 2005	1				8.2	3.7%
C4 Crater 1 2006	1				1.5	6.9%
C4 Crater 3 2004	1				23	3.5%
C4 Crater 3 2005	1				16	8.7%
C4 Crater 3 2006	1				3.9	0%

* One duplicate was below the detection limit. Detection limit (0.02 µg/g) was used to calculate mean of duplicates.

Table 21 (cont'd). Summary table comparing uncertainty associated with field samples and laboratory subsamples.

c. TNT						
Location	Number of field samples (n)	Mean of field samples (µg/g)	RSD (n ≥ 3)	RPD (n = 2)	Mean for lab duplicates	RPD for lab duplicates
Washington Range mortar impact point	2	0.07		143%*	0.12 <0.02	8.7% 0%
ERF 120-mm mortar low-order crater (0- to 3-cm depth)	1				2,870	0.7%
ERF 120-mm mortar low-order crater (3- to 6-cm depth)	1				209	1.0%
ERF 120-mm mortar low-order (30 m × 30 m) September 2005	3	1.32	60%		1.0 0.72 2.2	1.9% 1.4% 18%
ERF 120-mm mortar low-order (30 m × 30 m) May 2006	3	9.15	81%		4.3 5.4 18	0.2% 2.8% 5.6%
ERF 120-mm mortar low-order (30 m × 30 m) August 2006	4	0.45	105%		0.055 0.28 1.1 0.33	18% 18% 7.1% 6.1%
* One duplicate was below the detection limit. Detection limit (0.02 µg/g) was used to calculate mean of duplicates.						

Prior to 2005 when 120-mm mortar projectiles were fired into ERF, explosives residues from live-fire training were not detected in the impact area of Eagle River Flats, despite several sampling events by different agencies in the late 1980s through early 1990s (Racine et al. 1992, CH2MHill 1997). The 120-mm mortar apparently produces many more low-order detonations than the other munitions (60-mm and 81-mm mortar projectiles and 105-mm mortar projectiles) that have been fired into ERF over the last 20 years. Because these low-order detonations are relatively recent, the persistence of the HE residues should be monitored. The water-saturated, anaerobic conditions of the salt marsh that preserved WP particles should result in dissolution and biotransformation of RDX and TNT. In contrast, arid conditions, such as those found on parts of the Washington Range in the Donnelly Training Area, would enhance the persistence

of HE residues should a low-order detonation occur. HE residues have been detected sporadically on the Washington Range (Walsh et al. 2002, Bristol 2002), following the pattern typical of mortar and artillery impact areas where most of the surface soil does not contain detectable HE residues.

Areas with particulate explosives have proven to be extremely difficult to characterize by soil sampling as demonstrated in this report and elsewhere (Jenkins et al. 2005, Radtke et al. 2002). Nevertheless, the multi-increment sampling approach has been successful at accurately assessing HE mass at hand grenade ranges, anti-tank ranges, and demolition areas, but impact areas for artillery and mortar training have been more difficult to assess. When concentration estimates of replicate field samples do not agree within acceptable limits, inadequate sample mass and/or number of increments was obtained for the samples. Given that many of the samples we collected from impact areas were over 5 kg and made up of 100 or more increments, the extreme heterogeneity of the HE residue can be appreciated. The laboratory sample processing procedures that include air-drying, sieving through a 2-mm mesh, and particle size reduction by grinding for 60 to 90 s on a ring mill have reduced subsampling error so that it is insignificant compared to the field sampling uncertainty (Table 21).

6 Conclusions

The primary objective of these studies was to monitor the accumulation and/or persistence of energetic residues on Alaskan training ranges. At firing points that have been sampled iteratively since 2001, there does not appear to be significant accumulation of propellant residue. Specifically, 2,4-DNT has been consistently detected in the low parts-per-million concentration range in the surface soils. We have fewer data for NG, but it appears to occur at higher concentrations than 2,4-DNT, up to hundreds of parts per million, some of which may be the result of propellant burning, not firing activities.

High-explosives residues are more difficult to assess accurately due to greater compositional and distributional heterogeneity than propellant at firing points. Nonetheless, HE residues at upland sites are quite persistent and probably depend on the particle size distribution of the initial HE residue (large particles persisting longer). The HE residues from low-order detonations in the Eagle River Flats salt marsh show evidence of declining concentrations, but more multi-year data will be needed to determine whether the removal processes (dissolution and biotransformation) exceed the input of new HE residue.

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Appendix A: Sample Handling and Analytical Methods

General Laboratory Procedures for Soil Samples

All soil, sediment, and vegetation samples were air-dried by spreading them on polyethylene or aluminum-foil-covered trays at ambient temperature for several days. The air-dried samples that were predominately soil were sieved through a #10 mesh (2-mm) sieve to remove the oversize fraction consisting primarily of rocks and pebbles. Any dried surface vegetation was combined with the less-than-2-mm fraction that was further processed as described below. Samples that were highly organic (FP Sally and FP Bo-Whale) and sediment samples from Eagle River Flats were not sieved.

With the exception of samples from FP Mark, FP Sally, and FP Lampkin, and one sample from FP Fagan, multi-increment samples were ground on a ring mill in 500-g increments. The ring mill was a LabTech Essa (Belmont, Western Australia) LM-2 equipped with a B800 bowl. Firing point samples were ground for five 60-s cycles and impact area samples were ground for one 60- or 90-s cycle.

Ground multi-increment samples were manually subsampled. Each sample was spread over a flat surface and duplicate 10.0-g subsamples were formed from several small increments taken from random locations. Many increments were used to form each subsample because the multi-increment samples were ground in 500-g portions and each portion would not be expected to have the same analyte concentrations. Each 10-g sample was extracted with acetonitrile by shaking for 18 hours.

One sieved soil sample (FP Fagan) was divided using a LabTech Essa Rotary Sample Divider Model RSD5 to assess the uncertainty associated with splitting a large field sample. Each approximately 400-g split was extracted with 600 mL of acetonitrile by shaking for 18 hours.

Samples from FP Mark, FP Sally, and FP Lampkin were extracted with acetone using a whole-sample extraction procedure. This procedure was used to conform with the procedure used in 2003 and to allow direct comparison of concentration estimates without subsampling uncertainty. Each soil sample was weighed and transferred to a large polyethylene carboy. The volume of acetone added was

based on the mass of the sample; 2 L of acetone were used for each kilogram of sample. The carboy was capped and the sample shaken vigorously, then allowed to stand. The sample was shaken vigorously again a few hours later and again the following morning for a total extraction time of 18 to 20 hours. Then the sample was allowed to stand while the solids settled.

Water Samples

Water samples were preconcentrated using solid-phase extraction. Each Waters PoraPak RDX Sep-Pak Vac cartridge was preconditioned with 15 mL acetonitrile (gravity flow), then with 30 mL of reagent-grade water (Milli-Q) at less than 10 mL/min. A 500-mL water sample was passed through each cartridge at less than 10 mL/min, then each cartridge was dried under vacuum for at least 20 minutes to remove residual water. The dried cartridges were eluted with 5 mL of acetonitrile. Generally, 4.5 mL were recovered, so the final volume was made up to 5.0 mL with acetonitrile to yield a hundredfold concentration factor.

Analytical Methods

Energetic compounds were determined using HPLC-UV following the general procedures in USEPA Method 8330 (USEPA 1994). If compounds were not detectable by HPLC-UV, the extracts were analyzed by GC- μ ECD following USEPA Method 8095 (USEPA 2000).

Aliquots of the acetone and acetonitrile soil extracts were filtered through Millex-FH (Millipore, PTFE, 0.45- μ m) filter units into 7-mL Teflon-capped vials. Prior to HPLC analysis, 1.00 mL of each acetonitrile or acetone extract was mixed with 3.00 mL of reagent-grade water. Determinations were made on a modular system from Thermo Electron Corporations composed of a Finnigan SpectraSYSTEM Model P4000 pump, a Finnigan SpectraSYSTEM UV2000 dual wavelength UV/VS absorbance detector set at 210 (to detect NG) and 254 nm (cell path 1 cm), and a Finnigan SpectraSYSTEM AS300 autosampler. Samples were introduced with a 100- μ L sample loop. Separations were achieved on a 15-cm \times 3.9-mm (4- μ m) NovaPak C8 column (Waters Chromatography Division, Milford, Massachusetts) at 28°C and eluted with 1.4 mL/min of 15:85 isopropanol/water (v/v).

One set of soil extracts (FP Bondsteel) and the Lampkin Range water sample extracts were analyzed by GC- μ ECD. The acetonitrile extracts were transferred to autosampler vials that were then placed into an HP 7683 Series autosampler tray that was continuously refrigerated by circulating 0°C glycol/water through the

trays. A 1- μ L aliquot of each extract was directly injected into the HP 6890 purged packed inlet port (250°C) containing a deactivated Restek Uniliner. Separation was conducted on a 6-m- \times 0.53-mm-ID fused-silica column, with a 0.5- μ m film thickness of 5%-(phenyl)-methylsiloxane (RTX-5 from Restek). The GC oven was temperature-programmed as follows: 100°C for 2 min, 10°C/min ramp to 250°C. The carrier gas was hydrogen at 0.85 psi inlet pressure. The μ ECD detector temperature was 280°C; the makeup gas was nitrogen at 60 mL/min.

Calibration standards were prepared from analytical reference materials obtained from Restek Corporation (Bellefonte, Pennsylvania). The analytical reference materials were 8095 Calibration Mix A (HMX, RDX, TNT, 2,4-DNT, 2,6-DNT, 1,3-DNB, 1,3,5-TNB, 2-Am-4,6-DNT, 4-Am-2,6-DNT, and tetryl) and a single-component solution of NG; the concentration of each analyte was 1 mg/mL in acetonitrile. A 1- and a 10-mg/L solution were used to calibrate the HPLC-UV and a series of standards from 1 to 100 μ g/L was used to calibrate the GC- μ ECD. Soil concentrations were obtained by first calculating the extract concentrations. Extract concentrations were then multiplied by the volume of solvent used to extract each sample or subsample and divided by the mass of extracted soil. Extracts that had concentrations greater than 20 mg/L were diluted with acetonitrile prior to mixing with water and HPLC analysis.

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14. ABSTRACT Soil was collected from Alaskan firing points and impact areas to assess accumulation of 2,4-DNT, NG, RDX, TNT, and/or HMX resulting from live-fire training activities. At each sampling site, the energetic compound was known from previous sampling or from specific training events. Surface soils at firing points for 105-mm howitzers had part-per-million concentrations of 2,4-DNT resulting from deposition of slivers of propellant from multi-perforated single-base propellant grains. 2,4-DNT was not detectable at a 155-mm howitzer firing point where the propellant formulation was the same, but the propellant grain was single-perforated. Nitroglycerin was detected from tens to hundreds of parts per million at mortar firing points, some of which may have been due to burning of excess propellant. Consistent soil sampling depth to monitor propellant residues is important because 2,4-DNT and NG concentrations decrease sharply with depth. At vegetated firing points, propellant was detectable in mosses and dry, matted grasses, but not in recently emergent leafy vegetation. To estimate the concentration of high-explosives residues, more mass and increments are needed to overcome the greater spatial and compositional heterogeneity. Particulate HE can persist for many years at upland impact areas, but degradation processes are apparent in a salt marsh impact area.					
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